The end-to-end distribution function for a flexible chain with weak excluded-volume interactions

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Abstract

An explicit expression is derived for the distribution function of end-to-end vectors and for the mean square end-to-end distance of a flexible chain with excluded-volume interactions. The Hamiltonian for a flexible chain with weak intra-chain interactions is determined by two small parameters: the ratio ε of the energy of interaction between segments (within a sphere whose radius coincides with the cut-off length for the potential) to the thermal energy, and the ratio δ of the cut-off length to the radius of gyration for a Gaussian chain. Unlike conventional approaches grounded on the mean-field evaluation of the end-to-end distance, the Green function is found explicitly (in the first approximation with respect to ε). It is demonstrated that (i) the distribution function depends on ε in a regular way, while its dependence on δ is singular, and (ii) the leading term in the expression for the mean square end-to-end distance linearly grows with ε and remains independent of δ.

Key-words: Flexible chains, Excluded-volume interaction, Path integral, Distribution function

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1 Introduction

This paper is concerned with the distribution function of end-to-end vectors for a flexible chain with weak excluded-volume interactions. The effect of intra-chain interactions on the characteristic size of "real" flexible chains has attracted substantial attention from the beginning of the 50s of the past century, see early studies [1]–[7]. A noticeable progress has been reached in this area during the past five decades, see [8]–[24], to mention a few works, and the results of investigation have been summarized in a number of monographs [25]–[27]. Nevertheless, the effect of segment interactions on the statistics of macromolecules has remained a subject of debate in the past five years. This conclusion is confirmed by a large number of publications, where this phenomenon is discussed, see [28]–[41], and it may be ascribed to the importance of steric interactions for the description of such phenomena as (i) protein folding and denaturation [37], (ii) unzipping of DNA molecules [40], (iii) force–stretch relations for long chains at relatively small elongations [34], and (iv) transport of flexible chains through narrow pores [39]. The account for intra-chain interactions (i) provides a consistent description of the dependence of intrinsic viscosity on molecular weight in dilute polymer solutions [13, 15, 22], (ii) leads to an adequate characterization of time-dependent shear stresses in polymer fluids [20, 21, 22, 30, 33, 36, 38], (iii) allows transport coefficients in polymer melts to be correctly estimated [33], and (iv) predicts reinforcements of interfaces between incompatible solvents by random copolymers [29]. Interactions between segments are assumed to be responsible for (i) swelling of polymer gels [12, 24], (ii) mechanical [36, 38] and optical [22] anisotropy of polymer solutions, (iii) structure of polyelectrolyte chains [14, 19, 42], (iv) stability of globular proteins [23, 37], etc.

There are two conventional ways to describe excluded-volume interactions in a flexible chain. According to the first, a freely jointed chain is thought of as a set of rigid segments with given length linked in sequel, whereas the intra-chain interactions do not permit each pair of segments to occupy the same place. This model implies that the distribution function for end-to-end vectors coincides with that for a self-avoiding random walk. Although an explicit expression for the latter function is unknown, it is believed that the main term in the expansion of the distribution function for a long chain (with the number of segments $N \gg 1$) is described by either a stretched exponential function or a stretched exponential function multiplied by some power of the end-to-end distance [43, 44]. Results of numerical simulation confirm these hypotheses, but appropriate exponents are not precisely known [45].

According to the other method, a chain is treated as a sequence of beads bridged by (entropic) elastic springs [25]. The Hamiltonian of the system equals the sum of the conventional Hamiltonian for a Gaussian chain and the excluded-volume functional, where the energy of repulsive interactions between segments is approximated by the Dirac delta-function. To assess the effect of steric interactions on the mean square end-to-end distance, it is presumed that the intensity of interactions is small compared to thermal energy.

By applying various approximate techniques, the average end-to-end distance was evaluated in a number of studies (to the best of our knowledge, only a few attempts were undertaken to determine the distribution function of end-to-end vectors [8, 18]). It is widely accepted [25, 26] that (i) the mean square end-to-end distance B of a flexible chain with segment interactions is determined by some small dimensionless parameter ϵ (which quantity coincides with the product $\varepsilon\delta$ introduced later), (ii) the ratio $(B/b)^2$, where b is the mean square end-to-end distance for a Gaussian chain, may be expanded into a Taylor series in ϵ, and (iii) the leading term (proportional to ϵ) in this expansion is positive, which means that excluded-volume interactions are always repulsive. The common feature of the mathematical methods applied to develop these results was that all of them were grounded on the mean-field approach (the propagator for an appropriate path integral was

evaluated on the classical path only).

The objective of the present study is to develop an explicit expression for the distribution function of end-to-end vectors by evaluating the functional integral on (more or less) arbitrary paths (conformations of a chain). Our main result is that conclusions (i) to (iii) appear to be questionable. It is demonstrated that the Green function for a flexible chain with excluded-volume interactions is characterized by two small parameters, one of which, ε, describes the intensity of intra-chain interactions per small volume associated with the segment length, while the other, δ, determines the ratio of the segment length to the average end-to-end distance for a Gaussian chain. The difference between these parameters is that the dependence of the distribution function on ε is regular, whereas its dependence on δ is singular. It is found that the leading terms in the expression for the mean square end-to-end distance is proportional to ε, the scaling that substantially differs from the results of previous works. The growth of the average size of a chain with the intensity of segment interactions is ensured when the excluded-volume potential is included into the Hamiltonian with the sign different from the conventional one.

The exposition is organized as follows. A Hamiltonian for a flexible chain with excluded-volume interactions is discussed in Section 2. This Hamiltonian is calculated on the classical path in Section 3. Mean-field approximations for the Green function and the end-to-end distance are given in Section 4. A perturbed Hamiltonian is determined in Section 5. Our analysis is based on the conventional approach, according to which the excluded-volume potential is expanded in a Taylor series in the vicinity of the classical path up to quadratic terms (a similar technique was recently employed in [46] for the screened Coulomb potential). A leading term (with respect to small parameters) in the expression for the Green function is determined in Section 6. The mean square end-to-end distance B is evaluated in Section 7 for weak ($\varepsilon\delta^{-2} \ll 1$) and in Section 8 for moderately strong (arbitrary values of this ratio) interactions. Some concluding remarks are formulated in Section 9. Mathematical derivations are presented in Appendices A to F.

2 Formulation of the problem

A flexible chain is treated as a curve with "length" L in a three-dimensional space. An arbitrary configuration of the chain is determined by the function $\mathbf{r}(s)$, where $\mathbf{r}$ denotes radius vector and $s \in [0, L]$. For definiteness, we assume the end $s = 0$ to be fixed at the origin, $\mathbf{r}(0) = \mathbf{0}$, and the end $s = L$ to be free. An "internal structure" of the curve is characterized by a segment length b_0 and the number of segments $N \gg 1$, which are connected with length L by the formula $L = b_0 N$. In the absence of segment interactions, the Hamiltonian

$$H_0(\mathbf{r}) = \frac{3k_{\rm B}T}{2b_0}\int_0^L \Big(\frac{d\mathbf{r}}{ds}(s)\Big)^2 ds \tag{1}$$

is ascribed to the chain. Here $k_{\rm B}$ is Boltmann's constant, and T is the absolute temperature. The energy of intra-chain interactions is described by the functional

$$\bar{V}(\mathbf{r}) = \frac{v_0}{2L^2}\int_0^L ds \int_0^L V\Big(\mathbf{r}(s) - \mathbf{r}(s')\Big) ds', \tag{2}$$

where $V(\mathbf{r})$ is a dimensionless potential energy of interactions, and v_0 is their intensity (which is assumed to be positive for repulsive and negative for attractive interactions). We confine ourselves to isotropic functions $V(\mathbf{r}) = V_*(r)$ with $r = |\mathbf{r}|$. The entire Hamiltonian of the chain reads

$$H = H_0 + \bar{V}, \tag{3}$$

which implies that

$$H(\mathbf{r}) = k_{\rm B}T\Big[\frac{3}{2b_0}\int_0^L \Big(\frac{d\mathbf{r}}{ds}(s)\Big)^2 ds + \frac{v_0}{2k_{\rm B}TL^2}\int_0^L ds\int_0^L V\Big(\mathbf{r}(s)-\mathbf{r}(s')\Big)ds'\Big]. \tag{4}$$

Although Eq. (3) is employed in a number of studies, see [25] and the references therein, the sign of the second term in this formula seems questionable, because $\bar{V}$ may be considered as a work of some fictitious external field that prevents segments from being located at the same positions. The latter implies that the contribution of $\bar{V}$ into H should be negative (as, for example, that of the work of an external force at extension of a chain). We postpone a discussion of the sign of $\bar{V}$ to Section 7, and suppose at this stage that v_0 may have an arbitrary sign.

The Green function (propagator) for a chain $G(\mathbf{Q})$ is given by

$$G(\mathbf{Q}) = \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{Q}} \exp\Big[-\frac{H(\mathbf{r})}{k_{\rm B}T}\Big]\mathcal{D}(\mathbf{r}(s)), \tag{5}$$

where the path integral is calculated over all curves $\mathbf{r}(s)$ that obey the boundary conditions

$$\mathbf{r}(0)=\mathbf{0}, \qquad \mathbf{r}(L)=\mathbf{Q}. \tag{6}$$

The aim of this study is to develop an explicit expression for the Green function of a chain with relatively weak segment interactions, when the last term in Eq. (4) is "small" compared to the first. The derivation is performed for an arbitrary function $V(\mathbf{r})$, but our specific interest is in the excluded-volume potential $V(\mathbf{r}) = \hat{\delta}_{\rm D}(\mathbf{r})$, where $\delta_{\rm D}(\mathbf{r})$ denotes the Dirac delta-function, and $\hat{\delta}_{\rm D}(\mathbf{r})$ stands for its regularization after cut-off at small distances. To provide a rigorous definition, we introduce the Fourier transform of $V(\mathbf{r})$,

$$U(\mathbf{k}) = \int V(\mathbf{r})\exp(\imath\mathbf{k}\cdot\mathbf{r})d\mathbf{r} \tag{7}$$

with the inverse

$$V(\mathbf{r}) = \frac{1}{(2\pi)^3}\int U(\mathbf{k})\exp(-\imath\mathbf{k}\cdot\mathbf{r})d\mathbf{k}, \tag{8}$$

where the dot stands for inner product. Equation (7) implies that for an isotropic function $V(\mathbf{r})$, the function $U(\mathbf{k})$ is isotropic as well,

$$U(\mathbf{k}) = U_*(k), \qquad U_*(k) = \frac{4\pi}{k}\int_0^\infty V_*(r)\sin(kr)rdr.$$

The Fourier transform of the Dirac delta-function $\delta_{\rm D}(\mathbf{r})$ reads $U_{{\rm D}*}(k)=1$. To avoid divergence of the integral in Eq. (4), this function is cut off at an appropriate length-scale $b_* = k_*^{-1}$,

$$\hat{U}_{{\rm D}*}(k) = \left\{\begin{array}{ll} 1, & k\le k_*, \\ 0, & k > k_*, \end{array}\right. \tag{9}$$

and the potential $\hat{\delta}_{\rm D}(\mathbf{r})$ is defined as the inverse Fourier transform of $\hat{U}_{{\rm D}*}(k)$. To ensure that the potential $\hat{U}_{{\rm D}*}$ describes intra-chain interactions properly, we assume the length-scale of cut-off b_* to be substantially lower than the mean-square end-to-end distance for a Gaussian chain $b=\sqrt{b_0L}$,

$$\delta = \frac{b_*}{b} \ll 1. \tag{10}$$

3 Weak excluded-volume interactions

To characterize the "smallness" of the potential $\bar{V}$, we, first, introduce a test function $\mathbf{r}_0$ (the classical path) that minimizes functional (1) under conditions (6). Then the values of H_0 and $\bar{V}$ are determined on the curve $\mathbf{r}_0(s)$, and the dimensionless parameter ε is chosen from the condition that $\bar{V}(\mathbf{r}_0)$ is small compared with $H_0(\mathbf{r}_0)$ for any properly scaled end-to-end vector $\mathbf{Q}$. We introduce a Cartesian coordinate frame $\{x, y, z\}$, whose z axis is directed along the vector $\mathbf{Q}$, and present the minimization problem for the non-perturbed Hamiltonian H_0 as follows:

$$\min \int_0^L \Big[\Big(\frac{dx}{ds}(s)\Big)^2 + \Big(\frac{dy}{ds}(s)\Big)^2 + \Big(\frac{dz}{ds}(s)\Big)^2\Big] ds,$$
$$x(0) = y(0) = z(0) = 0, \quad x(L) = Q, \quad y(L) = z(L) = 0.$$

The unique solution of this problem is given by

$$\mathbf{r}_0(s) = \mathbf{Q}\frac{s}{L}. \tag{11}$$

It follows from Eqs. (1) and (11) that

$$H_0(\mathbf{r}_0) = \frac{3}{2} k_{\rm B} T \tilde{Q}^2, \qquad \tilde{Q} = \frac{Q}{b}. \tag{12}$$

Equation (8) implies that

$$V\Big(\mathbf{r}(s) - \mathbf{r}(s')\Big) = \frac{1}{(2\pi)^3} \int U(\mathbf{k}) \exp\Big[-\imath \mathbf{k} \cdot \Big(\mathbf{r}(s) - \mathbf{r}(s')\Big)\Big] d\mathbf{k}.$$

Substitution of this expression into Eq. (2) results in

$$\bar{V}(\mathbf{r}) = \frac{v_0}{2L^2(2\pi)^3} \int U(\mathbf{k}) d\mathbf{k} \int_0^L ds \int_0^L \exp\Big[-\imath \mathbf{k} \cdot \Big(\mathbf{r}(s) - \mathbf{r}(s')\Big)\Big] ds'. \tag{13}$$

Combining Eqs. (11) and (13), we find that

$$\bar{V}(\mathbf{r}_0) = \frac{v_0}{2L^2(2\pi)^3} \int U(\mathbf{k}) d\mathbf{k} \int_0^L ds \int_0^L \exp\Big(-\imath \mathbf{k} \cdot \mathbf{Q}\frac{s - s'}{L}\Big) ds'. \tag{14}$$

Simple algebra implies that (Appendix A)

$$\bar{V}(\mathbf{r}_0) = \frac{v_0}{2(\pi b\tilde{Q})^2} \int_0^1 \frac{dx}{x^2} \int_0^\infty U_*(k)\Big(1 - \cos(kb\tilde{Q}x)\Big) dk. \tag{15}$$

Formula (15) determines the energy of intra-chain interactions for an arbitrary function $U_*(k)$. In particular, for the excluded-volume potential (9), this equality reads

$$\bar{V}(\mathbf{r}_0) = \frac{v_0}{2(\pi b\tilde{Q})^2} \int_0^1 \frac{dx}{x^2} \int_0^{k_*} \Big(1 - \cos(kb\tilde{Q}x)\Big) dk. \tag{16}$$

Calculation of the integral (Appendix A) results in

$$\bar{V}(\mathbf{r}_0) = \frac{v_0 k_*^3}{4\pi^2} A(k_* b\tilde{Q}), \tag{17}$$

where

$$A(x) = \frac{1}{x^3}\int_0^x (x^2 - z^2)\frac{1 - \cos z}{z^2} dz. \tag{18}$$

The function $A(x)$ is plotted in Figure 1, which shows that A monotonically decreases with x. The limits of $A(x)$ as $x \to 0$ and $x \to \infty$ are given by (Appendix A)

$$\lim_{x\to 0} A(x) = \frac{1}{3}, \quad \lim_{x\to\infty} A(x) = 0. \tag{19}$$

It follows from Eqs. (12) and (17) that the smallness of the functional $\bar{V}$ compared with the non-perturbed Hamiltonian H_0 is tantamount to that of the pre-factor

$$\frac{v_0 k_*^3}{4\pi^2} = \frac{v_0}{3\pi\nu}$$

compared with thermal energy $k_B T$. Here $\nu = \frac{4}{3}\pi b_*^3$ is the volume in which interactions between segments are taken into account. Introducing the parameter ε by

$$\varepsilon = \frac{v_0}{k_B T \nu}, \tag{20}$$

we conclude that the condition $|\varepsilon| \ll 1$ means that the energy of excluded-volume interactions at the length-scale of cut-off is small compared with thermal energy. Substitution of expressions (12), (17) and (20) into Eq. (4) results in

$$H(\mathbf{r}_0) = k_B T\Big[\frac{3}{2}\tilde{Q}^2 + \frac{\varepsilon}{3\pi}A(\frac{\tilde{Q}}{\delta})\Big]. \tag{21}$$

According to Eq. (21), in the mean-field approximation, the functional H is determined by two dimensionless quantities, ε and δ. The former characterizes the smallness of excluded-volume interactions, whereas the latter describes the length-scale where these interactions are important. The parameter ε is located in the numerator, which means that it is responsible for regular perturbations of H_0, while δ stands in the denominator, which implies that it describes singular perturbations. This distinguishes the present approach from previous studies, where one small parameter was introduced, and its effect was assumed to be regular in the sense that the Green function was expanded into a Taylor series with respect to this quantity.

Before proceeding with the calculation of the Hamiltonian H on an arbitrary curve $\mathbf{r}(s)$, it is instructive to evaluate the Green function $G(\mathbf{Q})$ and its second moment on the classical path $\mathbf{r}_0(s)$.

4 Mean-field approximation of the Green function

Our aim is to find an approximation of the mean square end-to-end distance B when the set of admissible curves $\{\mathbf{r}(s)\}$ contains the classical path $\mathbf{r}_0(s)$ only. Substitution of expression (21) into Eq. (5) results in

$$G(\mathbf{Q}) = C\exp\Big[-\Big(\frac{3}{2}\tilde{Q}^2 + \frac{\varepsilon}{3\pi}A(\frac{\tilde{Q}}{\delta})\Big)\Big], \tag{22}$$

where the pre-factor C characterizes the measure $\mathcal{D}(\mathbf{r}(s))$ of the function $\mathbf{r}_0(s)$. To determine C, we treat the Green function as the distribution function of end-to-end vectors $\mathbf{Q}$ that obeys the normalization condition

$$\int G(\mathbf{Q})d\mathbf{Q} = 1.$$

In the spherical coordinate frame $\{Q, \phi, \theta\}$ whose z vector is directed along the vector $\mathbf{Q}$, this equality reads

$$4\pi \int_0^\infty G(Q) Q^2 dQ = 1. \tag{23}$$

Substituting expression (22) into Eq. (23) and setting $Q = b\tilde{Q}$, we find that

$$4\pi b^3 C \int_0^\infty \exp\Big[-\Big(\frac{3\tilde{Q}^2}{2} + \frac{\varepsilon}{3\pi} A(\frac{\tilde{Q}}{\delta})\Big)\Big] \tilde{Q}^2 d\tilde{Q} = 1.$$

Expanding the function under the integral into the Taylor series (this is possible because the function $A(x)$ is uniformly bounded) and disregarding terms beyond the first order of smallness with respect to ε, we obtain

$$4\pi b^3 C \int_0^\infty \exp\Big(-\frac{3\tilde{Q}^2}{2}\Big) \Big[1 - \frac{\varepsilon}{3\pi} A(\frac{\tilde{Q}}{\delta})\Big] \tilde{Q}^2 d\tilde{Q} = 1.$$

It follows from this equality that with the required level of accuracy,

$$C = \Big(\frac{3}{2\pi b^2}\Big)^{\frac{3}{2}} \Big(1 + \varepsilon \sqrt{\frac{6}{\pi^3}} C_1\Big), \tag{24}$$

where

$$C_1 = \int_0^\infty A(\frac{\tilde{Q}}{\delta}) \exp\Big(-\frac{3\tilde{Q}^2}{2}\Big) \tilde{Q}^2 d\tilde{Q}. \tag{25}$$

The leading term in the expression for C_1 reads (Appendix B)

$$C_1 = \frac{\pi\delta}{6}. \tag{26}$$

The mean square end-to-end distance of a chain is given by

$$B^2 = \int Q^2 G(\mathbf{Q}) d\mathbf{Q}.$$

In the spherical coordinates $\{Q, \phi, \theta\}$, this equality is presented in the form

$$B^2 = 4\pi \int_0^\infty G(Q) Q^4 dQ. \tag{27}$$

Substituting expression (22) into Eq. (27), introducing the new variable $\tilde{Q} = Q/b$, and neglecting terms beyond the first order of smallness with respect to ε, we find that

$$B^2 = 4\pi b^5 C \int_0^\infty \exp\Big(-\frac{3\tilde{Q}^2}{2}\Big) \Big[1 - \frac{\varepsilon}{3\pi} A(\frac{\tilde{Q}}{\delta})\Big] \tilde{Q}^4 d\tilde{Q}.$$

This equality implies that with the required level of accuracy,

$$\Big(\frac{B}{b}\Big)^2 = C\Big(\frac{2\pi b^2}{3}\Big)^{\frac{3}{2}} \Big(1 - \varepsilon \sqrt{\frac{6}{\pi^3}} B_1\Big), \tag{28}$$

where

$$B_1 = \int_0^\infty A(\frac{\tilde{Q}}{\delta}) \exp\Big(-\frac{3\tilde{Q}^2}{2}\Big) \tilde{Q}^4 d\tilde{Q}. \tag{29}$$

The leading term in the expression for B_1 reads (Appendix B)

$$B_1 = \frac{\pi\delta}{9}. \tag{30}$$

It follows from Eqs. (24), (26), (28) and (30) that

$$\Big(\frac{B}{b}\Big)^2 = 1 + \varepsilon\sqrt{\frac{6}{\pi^3}}(C_1 - B_1) = 1 + \frac{\varepsilon\delta}{9}\sqrt{\frac{3}{2\pi}}. \tag{31}$$

Equation (31) implies that at $v_0 > 0$, the mean square end-to-end distance of a flexible chain with excluded-volume interactions exceeds that of a Gaussian chain. At first sight, this conclusion confirms that the sign of the contribution of $\bar{V}$ into the Hamiltonian H is chosen correctly in Eq. (3). Setting $b_* = b_0$ (the cut-off of the potential U_* occurs at the segment length) and using Eqs. (10) and (20), we find that

$$\Big(\frac{B}{b}\Big)^2 = 1 + \frac{v_0}{\sqrt{6\pi}k_{\rm B}T\nu_{\rm tube}},$$

where $\nu_{\rm tube} = 4\pi b_0^2 b$ denotes volume of the characteristic tube around a chain (a circular cylinder whose radius coincides with the segment length and whose length equals the mean square end-to-end distance). Our aim now is to demonstrate that Eq. (31) does not capture the main contribution into the asymptotic expression for the average end-to-end distance. To prove this fact, we derive an explicit expression for the Hamiltonian H that accounts for second order terms with respect to admissible fluctuations from the classical path $\mathbf{r}_0(s)$.

5 Perturbations of the Hamiltonian

In accord with Eq. (6), the function $\mathbf{r}(s)$ is given by

$$\mathbf{r}(s) = \mathbf{Q}\frac{s}{L} + \mathbf{R}(s), \tag{32}$$

where the function $\mathbf{R}(s)$ satisfies the boundary conditions

$$\mathbf{R}(0) = \mathbf{0}, \qquad \mathbf{R}(L) = \mathbf{0}. \tag{33}$$

To simplify the analysis, we neglect longitudinal fluctuations and expand the function $\mathbf{R}(s)$ that describes transverse fluctuations into the Fourier series

$$\mathbf{R}(s) = \sum_{m=1}^{\infty} X_m \sin\frac{\pi m s}{L}\mathbf{e}_1 + \sum_{m=1}^{\infty} Y_m \sin\frac{\pi m s}{L}\mathbf{e}_2, \tag{34}$$

where X_m, Y_m are arbitrary coefficients, and $\mathbf{e}_k$ ($k = 1, 2, 3$) are unit vectors of a Cartesian coordinate frame, whose $\mathbf{e}_3$ vector is directed along the vector $\mathbf{Q}$. Any function $\mathbf{R}(s)$ obeying Eq. (34) satisfies also boundary conditions (33). We substitute expressions (32) and (34) into Eqs. (1) and (2) and, after some algebra, find that (Appendix C)

$$\begin{aligned} H_0(\mathbf{r}) &= H_0(\mathbf{r}_0) + \frac{3\pi^2 k_{\rm B}T}{4b^2}\sum_{m=1}^{\infty} m^2(X_m^2 + Y_m^2), \\ \bar{V}(\mathbf{r}) &= \bar{V}(\mathbf{r}_0) - \frac{v_0}{(4\pi)^2}\sum_{m,n=1}^{\infty} P_{mn}(X_m X_n + Y_m Y_n), \end{aligned} \tag{35}$$

where

$$
\begin{aligned}
P_{mn} \quad = \quad & \int_0^\infty U_*(k)k^4 dk \int_{-1}^{1}(1-x^2)dx\Big\{F(kQx) \\
& \times\Big[\cos\frac{\pi(m-n)}{2}\Big(F(kQx+\pi(m-n))+F(kQx-\pi(m-n))\Big) \\
& -\cos\frac{\pi(m+n)}{2}\Big(F(kQx+\pi(m+n))+F(kQx-\pi(m+n))\Big)\Big] \\
& -\cos\frac{\pi m}{2}\cos\frac{\pi n}{2}\Big[F(kQx+\pi m)-F(kQx-\pi m)\Big] \\
& \times\Big[F(kQx+\pi n)-F(kQx-\pi n)\Big]-\sin\frac{\pi m}{2}\sin\frac{\pi n}{2}\Big[F(kQx+\pi m) \\
& +F(kQx-\pi m)\Big]\Big[F(kQx+\pi n)+F(kQx-\pi n)\Big]\Big\},
\end{aligned}
\tag{36}
$$

and the function $F(z)$ reads

$$
F(z)=\frac{1}{z}\sin\frac{z}{2}. \tag{37}
$$

It follows from Eqs. (4) and (35) that with the required level of accuracy, the perturbed Hamiltonian H is given by

$$
H(\mathbf{r})=H(\mathbf{r}_0)+k_{\rm B}T\Big[\frac{3\pi^2}{4b^2}\sum_{m=1}^{\infty}m^2(X_m^2+Y_m^2)-\frac{\varepsilon\nu}{(4\pi)^2}\sum_{m,n=1}^{\infty}P_{mn}(X_mX_n+Y_mY_n)\Big]. \tag{38}
$$

Our purpose now is to substitute this expression into Eq. (5) and to calculate the path integral.

6 The Green function

Combining Eqs. (5) and (38), we find that

$$
\begin{aligned}
G(\mathbf{Q}) \quad = \quad & \exp\Big(-\frac{H(\mathbf{r}_0)}{k_{\rm B}T}\Big)\int_{\mathbf{R}(0)=\mathbf{0}}^{\mathbf{R}(L)=\mathbf{0}}\exp\Big\{-\frac{1}{2}\Big[\frac{3\pi^2}{2b^2}\sum_{m=1}^{\infty}m^2(X_m^2+Y_m^2) \\
& -\frac{\varepsilon\nu}{8\pi^2}\sum_{m,n=1}^{\infty}P_{mn}(X_mX_n+Y_mY_n)\Big]\Big\}\mathcal{D}(\mathbf{R}(s)).
\end{aligned}
\tag{39}
$$

Bearing in mind Eq. (21) and using the matrix presentation of the functional integral, we obtain

$$
G(\mathbf{Q})=C\exp\Big[-\Big(\frac{3\tilde{Q}^2}{2}+\frac{\varepsilon}{3\pi}A(\frac{\tilde{Q}}{\delta})\Big)\Big]\Lambda^2(\mathbf{Q}),\qquad \Lambda(\mathbf{Q})=\int\exp\Big[-\frac{1}{2}\mathbf{X}\cdot(\mathbf{A}+\varepsilon\mathbf{B})\cdot\mathbf{X}\Big]d\mathbf{X},
$$

where C is a constant associated with transition from the measure $\mathcal{D}(\mathbf{R}(s))$ to the measure $d\mathbf{X}$ (this quantity will be found from the normalization condition for the Green function). Here $\mathbf{X}$ is the vector with components X_m, $\mathbf{A}$ is the diagonal matrix with components $A_{mm}=3\pi^2m^2/(2b^2)$, and $\mathbf{B}$ is the matrix with components $B_{mn}=-\nu P_{mn}/(8\pi^2)$. Calculation of the Gaussian integral implies that

$$
G(\mathbf{Q})=C\exp\Big[-\Big(\frac{3\tilde{Q}^2}{2}+\frac{\varepsilon}{3\pi}A(\frac{\tilde{Q}}{\delta})\Big)\Big]\frac{\det\mathbf{A}}{\det(\mathbf{A}+\varepsilon\mathbf{B})}. \tag{40}
$$

In the first approximation with respect to ε,

$$
\det(\mathbf{A}+\varepsilon\mathbf{B})=\det\mathbf{A}\Big(1+\varepsilon\sum_{m=1}^{\infty}\frac{B_{mm}}{A_{mm}}\Big). \tag{41}
$$

It follows from Eqs. (40) and (41) that

$$G(\mathbf{Q}) = C\exp\Big[-\Big(\frac{3\tilde{Q}^2}{2} + \frac{\varepsilon}{3\pi}A(\tilde{Q})\Big)\Big]\Big(1 + \frac{\varepsilon\nu b^2}{12\pi^4}S\Big)^{-1}, \tag{42}$$

where

$$S = -\sum_{m=1}^{\infty}\frac{P_{mm}}{m^2}. \tag{43}$$

Substitution of expression (36) into Eq. (43) implies that (Appendix D)

$$S = \int_0^\infty U_*(k)k^4 dk \int_{-1}^1 (1-x^2)S_0(kQx)dx, \tag{44}$$

where

$$\begin{aligned} S_0(z) &= F(z)s_1(z) + s_2(z) - 2s_3(z) - \frac{\pi^2}{3}F^2(z), \\ s_1(z) &= \sum_{m=1}^{\infty}\frac{(-1)^m}{m^2}\Big[F(z+2\pi m) + F(z-2\pi m)\Big], \\ s_2(z) &= \sum_{m=1}^{\infty}\frac{1}{m^2}\Big[F^2(z+\pi m) + F^2(z-\pi m)\Big], \\ s_3(z) &= \sum_{m=1}^{\infty}\frac{(-1)^m}{m^2}F(z+\pi m)F(z-\pi m). \end{aligned} \tag{45}$$

The infinite sums are calculated in Appendix D, where it is shown that

$$S_0(z) = \frac{\pi^2}{2z^2}\alpha(z), \qquad \alpha(z) = 1 + 2\frac{\sin z}{z} - 6\frac{1-\cos z}{z^2}. \tag{46}$$

It follows from Eq. (46) that $S_0(z)$ is an even function. Using this property, we present Eq. (44) in the form

$$S = \frac{\pi^2}{Q^2}\int_0^1 \frac{1-x^2}{x^2}dx \int_0^\infty U_*(k)\alpha(kQx)k^2 dk. \tag{47}$$

Formula (47) determines the denominator in Eq. (42) for an arbitrary isotropic potential $V(\mathbf{r})$. For the function $U_{\mathrm{D}*}(k)$ given by Eq. (9), this equality reads (Appendix D)

$$S = \frac{\pi^2 k_*^5}{4}A_0\Big(\frac{\tilde{Q}}{\delta}\Big), \tag{48}$$

where

$$A_0(x) = \frac{1}{x^5}\int_0^x (x^2 - z^2)^2\frac{\alpha(z)}{z^2}dz. \tag{49}$$

The function $A_0(x)$ is plotted in Figure 1. This function is even, it is negative for any $x \in (-\infty, \infty)$, and it monotonically increases with $|x|$. The limits of the function $A_0(x)$ are given by (Appendix D)

$$\lim_{x\to 0} A_0(x) = -\frac{2}{45}, \qquad \lim_{x\to\infty} A_0(x) = 0. \tag{50}$$

It follows from Eqs. (42) and (48) that

$$G(\mathbf{Q}) = C\exp\Big[-\Big(\frac{3\tilde{Q}^2}{2} + \frac{\varepsilon}{3\pi}A(\frac{\tilde{Q}}{\delta})\Big)\Big]\Big[1 + \frac{\varepsilon}{36\pi\delta^2}A_0(\frac{\tilde{Q}}{\delta})\Big]^{-1}. \tag{51}$$

Equation (51) provides an analytical expression (up to the normalization constant C) for the Green function of a flexible chain with excluded-volume interactions. The only assumption employed in the derivation of this formula is the smallness of ε compared with unity (no limitations on δ were imposed). Given a coefficient δ, Eq. (51) is valid provided that the expression in the last square brackets does not vanish.

Our purpose now is to determine the normalization constant C and the mean square end-to-end distance B. We begin with the case of "weak" interactions when the dimensionless parameter $\varepsilon\delta^{-2}$ (and, as a consequence, ε) is small compared with unity.

7 Weak segment interactions

To determine the normalization constant C, we substitute expression (51) into Eq. (23) and obtain

$$4\pi b^3 C\int_0^\infty \exp\Bigl[-\Bigl(\frac{3\tilde{Q}^2}{2}+\frac{\varepsilon}{3\pi}A(\frac{\tilde{Q}}{\delta})\Bigr)\Bigr]\Bigl[1+\frac{\varepsilon}{36\pi\delta^2}A_0(\frac{\tilde{Q}}{\delta})\Bigr]^{-1}\tilde{Q}^2 d\tilde{Q}=1.$$

Expanding the function under the integral into the Taylor series and neglecting terms beyond the first order of smallness with respect to ε and $\varepsilon\delta^{-2}$, we find that

$$4\pi b^3 C\int_0^\infty \exp\Bigl(-\frac{3\tilde{Q}^2}{2}\Bigr)\Bigl\{1-\frac{\varepsilon}{3\pi}\Bigl[A(\frac{\tilde{Q}}{\delta})+\frac{1}{12\delta^2}A_0(\frac{\tilde{Q}}{\delta})\Bigr]\Bigr\}\tilde{Q}^2 d\tilde{Q}=1.$$

It follows from this equality that with the required level of accuracy,

$$C=\Bigl(\frac{3}{2\pi b^2}\Bigr)^{\frac{3}{2}}\Bigl[1+\varepsilon\sqrt{\frac{6}{\pi^3}}\Bigl(C_1+\frac{1}{12\delta^2}C_2\Bigr)\Bigr], \tag{52}$$

where C_1 is given by Eq. (25), and

$$C_2=\int_0^\infty A_0(\frac{\tilde{Q}}{\delta})\exp\Bigl(-\frac{3\tilde{Q}^2}{2}\Bigr)\tilde{Q}^2 d\tilde{Q}. \tag{53}$$

The leading term in the expression for C_2 reads (see Appendix E for detail)

$$C_2=-\frac{4}{3}\sqrt{\frac{2\pi}{3}}\delta^2. \tag{54}$$

Substituting expressions (26) and (54) into Eq. (52) and neglecting terms beyond the first order of smallness, we arrive at the formula

$$C=\Bigl(\frac{3}{2\pi b^2}\Bigr)^{\frac{3}{2}}\Bigl(1-\frac{2\varepsilon}{9\pi}\Bigr). \tag{55}$$

To calculate the mean square end-to-end distance B, we substitute expression (51) into Eq. (27), set $\tilde{Q}=Q/b$, disregard terms beyond the first order of smallness with respect to ε and $\varepsilon\delta^{-2}$, and find that

$$B^2=4\pi b^5 C\int_0^\infty \exp\Bigl(-\frac{3\tilde{Q}^2}{2}\Bigr)\Bigl\{1-\frac{\varepsilon}{3\pi}\Bigl[A(\frac{\tilde{Q}}{\delta})+\frac{1}{12\delta^2}A_0(\frac{\tilde{Q}}{\delta})\Bigr]\Bigr\}\tilde{Q}^4 d\tilde{Q}.$$

It follows from this equality that

$$\Bigl(\frac{B}{b}\Bigr)^2=C\Bigl(\frac{2\pi b^2}{3}\Bigr)^{\frac{3}{2}}\Bigl[1-\varepsilon\sqrt{\frac{6}{\pi^3}}\Bigl(B_1+\frac{1}{12\delta^2}B_2\Bigr)\Bigr], \tag{56}$$

where B_1 is given by Eq. (29), and

$$B_2 = \int_0^\infty A_0(\frac{\tilde{Q}}{\delta}) \exp\Bigl(-\frac{3\tilde{Q}^2}{2}\Bigr)\tilde{Q}^4 d\tilde{Q}. \tag{57}$$

The leading term in the expression for B_2 reads (Appendix E)

$$B_2 = -\frac{4}{9}\sqrt{\frac{2\pi}{3}}\delta^2. \tag{58}$$

Substituting expressions (30), (55) and (58) into Eq. (56) and neglecting terms beyond the first order of smallness, we find that

$$\Bigl(\frac{B}{b}\Bigr)^2 = C\Bigl(\frac{2\pi b^2}{3}\Bigr)^{\frac{3}{2}}\Bigl(1 + \frac{2\varepsilon}{27\pi}\Bigr) = 1 - \frac{4\epsilon}{27\pi}. \tag{59}$$

With reference to the conventional standpoint [the positive contribution of $\bar{V}$ into the Hamiltonian H in Eq. (3)] Eq. (59) contradicts our intuition: repulsive interactions between segments result in a decrease in the end-to-end distance. Formula (59) contradicts also the mean-field Eq. (31): the ratio $(B/b)^2$ is proportional to ε instead of the classical scaling $\varepsilon\delta$.

The latter discrepancy may be explained if we recall that excluded-volume interactions do not permit different segments of a flexible chain to occupy the same positions, which means that their effect is substantial only for "curved" configurations of a chain, whereas the mean-field approach is confined to "straight" configurations. This implies that the mean-field technique is inapplicable to the analysis of a flexible chain with long-range interactions between segments, in agreement with the conclusion derived about 50 years ago [2] (based on different arguments).

Equation (59) leads to a physically plausible result (an increase in the average end-to-end distance with intensity of excluded-volume interactions) when ε is negative. The latter is tantamount to the negativity of contribution of $\bar{V}$ into the Hamiltonian H in Eq. (3). To demonstrate the correctness of this assertion, it is instructive to compare the values of H on two paths: (P1) a straight line (11) that connects the end-points, and (P2) a sinusoidal path (32) and (34) with the only non-zero term corresponding to a fixed $m \geq 1$. According to the physical meaning of excluded-volume interactions, the energy H_2 on path (P2) should exceed the energy H_1 on the straight path (P1) as $\mathbf{Q} \to \mathbf{0}$, i.e., when the chain is superposed on itself several times. On the other hand, it follows from Eq. (35) that

$$H_2 = H_1 + \Bigl[\frac{3\pi^2 k_{\rm B}T}{4b^2} - \frac{v_0}{(4\pi)^2}\int_0^\infty \hat{U}_{{\rm D}*}(k)k^4 dk \int_{-1}^1 (1-x^2)p_{mm}(kQx)dx\Bigr](X_m^2 + Y_m^2), \tag{60}$$

where p_{mm} is given by Eq. (C-29). The integral in Eq. (60) can be calculated explicitly, but this is not necessary for our purpose, because Eq. (C-29) implies that in the limit of at small Q, the function p_{mm} reads

$$p_{mm}(kQx) \approx L^2.$$

Combining this estimate with Eq. (60), we see that Eq. (3) with the positive contribution of $\bar{V}$ results in $H_2 < H_1$ for sufficiently large v_0, which contradicts the definition of excluded-volume interactions.

Based on this analysis, we conclude that the potential of intra-chain interactions should be included into Eq. (3) with the negative sign, and, as a consequence, the distribution function of end-to-end vectors (51) should read

$$G(\mathbf{Q}) = C\exp\Bigl[-\frac{3\tilde{Q}^2}{2} + \frac{2}{3}\mu\delta^2 A(\frac{\tilde{Q}}{\delta})\Bigr]\Bigl[1 + \mu A_1(\frac{\tilde{Q}}{\delta})\Bigr]^{-1}, \tag{61}$$

where we introduce the notation

$$\mu = \frac{\varepsilon}{2\pi\delta^2}, \qquad A_1(x) = -\frac{1}{18}A_0(x) \tag{62}$$

and preserve the positiveness of $\varepsilon \ll 1$. We intend now to derive explicit expressions for the normalization constant C and the mean square end-to-end distance B for an arbitrary (non necessary small) values of the dimensionless parameter μ. Our aim is to demonstrate that Eqs. (55) and (59) provide the leading terms in the expressions for C and B (after an appropriate corrections of signs) when the condition $\varepsilon\delta^{-2} \ll 1$ is violated.

8 Moderately strong interactions

It follows from Eqs. (23) and (61) that

$$4\pi b^3 C \int_0^\infty \exp\Bigl(-\frac{3x^2}{2}\Bigr)\frac{1+\frac{2}{3}\mu\delta^2 A(\frac{x}{\delta})}{1+\mu A_1(\frac{x}{\delta})}x^2 dx = 1.$$

Bearing in mind that

$$\frac{1+\frac{2}{3}\mu\delta^2 A(\frac{x}{\delta})}{1+\mu A_1(\frac{x}{\delta})} = 1 - \mu\frac{A_1(\frac{x}{\delta}) - \frac{2}{3}\delta^2 A(\frac{x}{\delta})}{1+\mu A_1(\frac{x}{\delta})},$$

we find that

$$C = \Bigl(\frac{3}{2\pi b^2}\Bigr)^{\frac{3}{2}}\Bigl[1 - 6\mu\sqrt{\frac{3}{2\pi}}\int_0^\infty \frac{A_1(\frac{x}{\delta}) - \frac{2}{3}\delta^2 A(\frac{x}{\delta})}{1+\mu A_1(\frac{x}{\delta})}\Bigl(-\frac{3x^2}{2}\Bigr)x^2 dx\Bigr]^{-1}. \tag{63}$$

Evaluating the integrals

$$\Lambda_1 = \int_0^\infty \frac{A_1(\frac{x}{\delta})}{1+\mu A_1(\frac{x}{\delta})}\Bigl(-\frac{3x^2}{2}\Bigr)x^2 dx, \qquad \Lambda_2 = \int_0^\infty \frac{A(\frac{x}{\delta})}{1+\mu A_1(\frac{x}{\delta})}\Bigl(-\frac{3x^2}{2}\Bigr)x^2 dx, \tag{64}$$

and neglecting small terms, we arrive at the formula (see Appendix F for detail)

$$C = \Bigl(\frac{3}{2\pi b^2}\Bigr)^{\frac{3}{2}}\Bigl\{1 + \frac{\varepsilon}{\pi}\Bigl[\frac{2}{9} - \Bigl(\frac{3}{2\pi}\Bigr)^{\frac{3}{2}}\frac{\varepsilon}{\delta}\int_0^\infty \frac{A_1^2(x)x^2}{1+\mu A_1(x)}dx\Bigr]\Bigr\}. \tag{65}$$

Substituting Eq. (61) into Eq. (27), we find that

$$\Bigl(\frac{B}{b}\Bigr)^2 = \Bigl(\frac{2\pi b^2}{3}\Bigr)^{\frac{3}{2}}C\Bigl[1 - 3\sqrt{\frac{6}{\pi}}\mu\int_0^\infty \frac{A_1(\frac{x}{\delta}) - \frac{2}{3}\delta^2 A(\frac{x}{\delta})}{1+\mu A_1(\frac{x}{\delta})}\Bigl(-\frac{3x^2}{2}\Bigr)x^4 dx\Bigr]. \tag{66}$$

The integrals

$$\Gamma_1 = \int_0^\infty \frac{A_1(\frac{x}{\delta})}{1+\mu A_1(\frac{x}{\delta})}\Bigl(-\frac{3x^2}{2}\Bigr)x^4 dx, \qquad \Gamma_2 = \int_0^\infty \frac{A(\frac{x}{\delta})}{1+\mu A_1(\frac{x}{\delta})}\Bigl(-\frac{3x^2}{2}\Bigr)x^4 dx \tag{67}$$

are calculated in Appendix F, where it is shown that the leading term in the expression for the mean-square end-to-end distance B is given by

$$\Bigl(\frac{B}{b}\Bigr)^2 = \Bigl(\frac{2\pi b^2}{3}\Bigr)^{\frac{3}{2}}C\Bigl\{1 - \frac{2\varepsilon}{27\pi}\Bigl[1 + \frac{81}{8\pi^2}\sqrt{\frac{3}{2\pi}}\frac{\varepsilon^2}{\delta}\int_0^\infty \frac{A_1^3(x)x^4}{1+\mu A_1(x)}dx\Bigr]\Bigr\}. \tag{68}$$

Equations (65) and (68) imply that the leading term in the expression for the mean square end-to-end distance reads

$$\Big(\frac{B}{b}\Big)^2 = 1+\frac{\varepsilon}{\pi}\Big[\frac{4}{27}-\Big(\frac{3}{2\pi}\Big)^{\frac{3}{2}}\frac{\varepsilon}{\delta}\int_0^\infty \frac{A_1^2(x)x^2}{1+\mu A_1(x)}dx\Big]. \tag{69}$$

Formulas (65) and (69) differ from Eqs. (55) and (59), respectively, by the integral terms in the square brackets only (after correction of the sign of ε). Although these terms contain the pre-factor ε/δ which may accept arbitrary values, simple algebra demonstrates (Appendix F) that their contributions are negligible.

9 Concluding remarks

The formula

$$G(\mathbf{Q}) = \Big(\frac{3}{2\pi b^2}\Big)^{\frac{3}{2}}\Big(1+\frac{2\varepsilon}{9\pi}\Big)\exp\Big[-\frac{3Q^2}{2b^2}+\frac{\varepsilon}{3\pi}A\Big(\frac{Q}{\delta b}\Big)\Big]\Big[1+\frac{\varepsilon}{2\pi\delta^2}A_1\Big(\frac{Q}{\delta b}\Big)\Big]^{-1}$$

has been derived for the distribution function of end-to-end vectors for a flexible chain with weak excluded-volume interactions. Here b is the mean square end-to-end distance for a Gaussian chain, ε is a small parameter that describes the intensity of segment interactions, δ is the ratio of the average end-to-end distance for a Gaussian chain to its segment length, and the functions $A(x)$ and $A_1(x)$ are given by Eqs. (62), (A-8) and (D-24). The leading term in the expression for the mean square end-to-end distance reads

$$\Big(\frac{B}{b}\Big)^2 = 1+\frac{4\varepsilon}{27\pi}. \tag{70}$$

Equation (70) differs from similar relations developed in previous studies, where the ratio on the left-hand side was found to be proportional to $\varepsilon\delta$. A reason for this difference is that our result is grounded on the calculation of an appropriate path integral, whereas conventional conclusions are obtained by using mean-field approximations. It appears that the latter approach is inapplicable to problems where interactions between segments located far away (along a chain) from each other are substantial, because the mean-field technique is confined to "straight" paths only, while inter-chain interactions reveal themselves mainly on "curved" configurations of a chain.

It has been found in the calculation of the path integral that the sign of the excluded-volume potential should be corrected in the conventional formula (3) for the Hamiltonian. It has also been shown that the mean square end-to-end distance cannot be expanded into a Taylor series with respect to small parameters (as it is traditionally presumed), because even sub-leading terms of the highest order in the formula for B^2 include $\delta\ln\delta$, see Eq. (E-11), and $\sqrt{\varepsilon}$, see Eq. (F-25).

This work focuses on the analysis of the distribution function for a flexible chain with excluded-volume potential (9). However, the results can be easily extended to an arbitrary potential of intra-chain interactions by using Eqs. (15) and (47). In particular, these relations allow an explicit formula to be derived for the distribution function of end-to-end vectors for flexible polyelectrolyte chains. The latter will be the subject of a subsequent publication.

Appendix A

To transform integral (14), we choose a spherical coordinate frame $\{k, \phi, \theta\}$, whose z axis is directed along the vector $\mathbf{Q}$, and obtain

$$\bar{V}(\mathbf{r}_0) = \frac{v_0}{2L^2(2\pi)^3} \int_0^\infty U_*(k)k^2 dk \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^L ds \int_0^L \exp\Bigl(-\imath kQ\cos\theta \frac{s-s'}{L}\Bigr) ds'.$$

Calculating the integral over ϕ and introducing the new variable $x = \cos\theta$, we find that

$$\bar{V}(\mathbf{r}_0) = \frac{v_0}{L^2(2\pi)^2} \int_0^\infty U_*(k)k^2 dk \int_0^1 J(kQx)dx, \tag{A-1}$$

where

$$J(z) = \int_0^L ds \int_0^L \exp\Bigl(-\imath z\frac{s-s'}{L}\Bigr) ds' = \int_0^L \exp\Bigl(-\frac{\imath zs}{L}\Bigr) ds \int_0^L \exp\Bigl(\frac{\imath zs'}{L}\Bigr) ds'. \tag{A-2}$$

For an arbitrary non-negative z, we have

$$\int_0^L \exp\Bigl(-\frac{\imath zs}{L}\Bigr) ds = \frac{L}{\imath z}\Bigl(1-\exp(-\imath z)\Bigr), \qquad \int_0^L \exp\Bigl(\frac{\imath zs'}{L}\Bigr) ds' = \frac{L}{\imath z}\Bigl(\exp(\imath z)-1\Bigr), \tag{A-3}$$

It follows from Eqs. (A-2) and (A-3) that

$$J(z) = \frac{2L^2}{z^2}(1-\cos z). \tag{A-4}$$

Substitution of Eq. (A-4) into Eq. (A-1) implies (after changing the order of integration) that

$$\bar{V}(\mathbf{r}_0) = \frac{v_0}{2\pi^2 Q^2} \int_0^1 \frac{dx}{x^2} \int_0^\infty U_*(k)\Bigl(1-\cos(kQx)\Bigr) dk. \tag{A-5}$$

Combining Eqs. (12) and (A-5), we arrive at Eq. (15).

Introducing the new variable $z = kb\tilde{Q}x$, we find from Eq. (16) that

$$\bar{V}(\mathbf{r}_0) = \frac{v_0}{2\pi^2 (b\tilde{Q})^3} \int_0^1 \frac{dx}{x^3} \int_0^{k_* b\tilde{Q}x} (1-\cos z) dz.$$

Setting $y = k_* b\tilde{Q}x$, we obtain

$$\bar{V}(\mathbf{r}_0) = \frac{v_0 k_*^2}{2\pi^2 b\tilde{Q}} \int_0^{k_* b\tilde{Q}} \frac{dy}{y^3} \int_0^y (1-\cos z) dz.$$

We now change the order of integration

$$\bar{V}(\mathbf{r}_0) = \frac{v_0 k_*^2}{2\pi^2 b\tilde{Q}} \int_0^{k_* b\tilde{Q}} (1-\cos z) dz \int_z^{k_* b\tilde{Q}} \frac{dy}{y^3}, \tag{A-6}$$

and calculate the internal integral

$$\int_z^{k_* b\tilde{Q}} \frac{dy}{y^3} = \frac{(k_* b\tilde{Q})^2 - z^2}{2z^2 (k_* b\tilde{Q})^2}.$$

Substitution of this expression into Eq. (A-6) implies Eqs. (17) and (18).

To determine the limits of the function $A(x)$, we transform Eq. (18) as follows:

$$A(x) = \frac{1}{x} \int_0^x \frac{1 - \cos z}{z^2} dz - \frac{1}{x^3} \int_0^x (1 - \cos z) dz. \tag{A-7}$$

The first integral is simplified by integration by parts,

$$\int_0^x \frac{1 - \cos z}{z^2} dz = \frac{x - \sin x}{x^2} + 2 \int_0^x \frac{z - \sin z}{z^3} dz.$$

Calculation of the second integral in Eq. (A-7) implies that

$$\int_0^x (1 - \cos z) dz = x - \sin x.$$

Substitution of these expressions into Eq. (A-7) yields

$$A(x) = \frac{2}{x} \int_0^x a(z) dz, \qquad a(z) = \frac{z - \sin z}{z^3}. \tag{A-8}$$

To find limits of the function $A(x)$ as $x \to 0$ and $x \to \infty$, we apply L'Hospital's rule

$$\lim_x A(x) = \frac{2}{3} \lim_x \frac{1 - \cos x}{x^2}. \tag{A-9}$$

Equation (A-9) implies that

$$\lim_{x \to 0} A(x) = \frac{1}{3} \lim_{x \to 0} \frac{\sin x}{x} = \frac{1}{3},$$

which coincides with the first equality in Eq. (19). The other equality follows from Eq. (A-9).

Appendix B

Equation (24) follows from Eq. (23) and the formula

$$\int_0^\infty \exp\Big(-\frac{3\tilde{Q}^2}{2}\Big) \tilde{Q}^2 d\tilde{Q} = \frac{1}{6} \sqrt{\frac{2\pi}{3}}. \tag{B-1}$$

To determine the constant C_1, we substitute Eq. (A-8) into Eq. (25), introduce the new variable $x = \tilde{Q}/\delta$, change the order of integration, and find that

$$C_1 = 2\delta^3 \int_0^\infty a(z) dz \int_z^\infty \exp\Big(-\frac{3}{2}\delta^2 x^2\Big) x dx.$$

Calculating the internal integral,

$$\int_z^\infty \exp\Big(-\frac{3}{2}\delta^2 x^2\Big) x dx = \frac{1}{3\delta^2} \exp\Big(-\frac{3}{2}\delta^2 z^2\Big), \tag{B-2}$$

and setting $x = \delta z$, we arrive at

$$C_1 = \frac{2}{3}\delta \int_0^\infty \exp\Big(-\frac{3}{2}\delta^2 z^2\Big) a(z) dz = \frac{2}{3} \int_0^\infty a\Big(\frac{x}{\delta}\Big) \exp\Big(-\frac{3x^2}{2}\Big) dx.$$

It follows from Eq. (A-8) that the function $a(x)$ is even, which implies that

$$C_1 = \frac{1}{3} \int_{-\infty}^\infty a\Big(\frac{x}{\delta}\Big) \exp\Big(-\frac{3x^2}{2}\Big) dx. \tag{B-3}$$

As the limit of the function $a(x)$ as $x \to 0$ is finite and this function decreases being proportional to x^{-2} as $x \to \infty$, the Fourier transform

$$\hat{a}(s) = \int_{-\infty}^{\infty} a(x) \exp(\imath s x) dx \tag{B-4}$$

exists, and

$$a(\frac{x}{\delta}) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \hat{a}(s) \exp\Big(-\frac{\imath s x}{\delta}\Big) ds. \tag{B-5}$$

Substituting expression (B-5) into Eq. (B-3) and changing the order of integration, we obtain

$$C_1 = \frac{1}{6\pi} \int_{-\infty}^{\infty} \hat{a}(s) ds \int_{-\infty}^{\infty} \exp\Big[-\Big(\frac{3x^2}{2} + \frac{\imath s x}{\delta}\Big)\Big] dx. \tag{B-6}$$

To calculate the internal integral, we set $y = x\sqrt{3}$ and find that

$$\int_{-\infty}^{\infty} \exp\Big[-\Big(\frac{3x^2}{2} + \frac{\imath s x}{\delta}\Big)\Big] dx = \sqrt{\frac{2\pi}{3}} \exp\Big(-\frac{s^2}{6\delta^2}\Big). \tag{B-7}$$

Substituting expression (B-7) into Eq. (B-6) and introducing the new variable $x = 3/(\delta\sqrt{3})$, we obtain

$$C_1 = \frac{\delta}{3\sqrt{2\pi}} \int_{-\infty}^{\infty} \hat{a}(\delta x\sqrt{3}) \exp\Big(-\frac{x^2}{2}\Big) dx. \tag{B-8}$$

If the function $\hat{a}(s)$ have had finite derivatives at $s = 0$, the integral were evaluated up to an arbitrary level of accuracy with respect to δ by the stationary phase method. As this is not the case, we present Eq. (B-8) in the form

$$C_1 = \frac{\delta}{3\sqrt{2\pi}} \Big[\int_{-\infty}^{\infty} \hat{a}(0) \exp\Big(-\frac{x^2}{2}\Big) dx + \int_{-\infty}^{\infty} \Big(\hat{a}(\delta x\sqrt{3}) - \hat{a}(0)\Big) \exp\Big(-\frac{x^2}{2}\Big) dx\Big],$$

calculate the first integral,

$$C_1 = \frac{\delta}{3}\hat{a}(0) + R_1, \tag{B-9}$$

and evaluate the residual

$$R_1 = \frac{\delta}{3\sqrt{2\pi}} \int_{-\infty}^{\infty} \Big(\hat{a}(\delta s\sqrt{3}) - \hat{a}(0)\Big) \exp\Big(-\frac{s^2}{2}\Big) ds. \tag{B-10}$$

It follows from Eq. (B-4) that

$$\hat{a}(\delta s\sqrt{3}) - \hat{a}(0) = \int_{-\infty}^{\infty} a(x) \Big[\exp(\imath\delta s x\sqrt{3}) - 1\Big] dx.$$

As the function $a(x)$ is even, this equality reads

$$\hat{a}(\delta s\sqrt{3}) - \hat{a}(0) = \int_{-\infty}^{\infty} a(x) \Big[\cos(\delta s x\sqrt{3}) - 1\Big] dx = -4 \int_{0}^{\infty} a(x) \sin^2 \frac{\delta s x\sqrt{3}}{2} dx.$$

Substitution of Eq. (A-8) into this formula results in

$$\hat{a}(\delta s\sqrt{3}) - \hat{a}(0) = -3\delta^2 s^2 \int_{0}^{\infty} \Big(\frac{\sin\frac{\delta s x\sqrt{3}}{2}}{\frac{\delta s x\sqrt{3}}{2}}\Big)^2 \Big(1 - \frac{\sin x}{x}\Big) dx.$$

It follows from this equality that

$$|\hat{a}(\delta s\sqrt{3}) - \hat{a}(0)| \leq 3\delta^2 s^2 \int_0^\infty \Big(\frac{\sin\frac{\delta s x\sqrt{3}}{2}}{\frac{\delta s x\sqrt{3}}{2}}\Big)^2 \Big|1 - \frac{\sin x}{x}\Big| dx$$

$$\leq 6\delta^2 s^2 \int_0^\infty \Big(\frac{\sin\frac{\delta s x\sqrt{3}}{2}}{\frac{\delta s x\sqrt{3}}{2}}\Big)^2 dx = 4\delta|s|\sqrt{3} \int_0^\infty \Big(\frac{\sin y}{y}\Big)^2 dy = 2\pi\delta|s|\sqrt{3}. \qquad \text{(B-11)}$$

where we set $y = \frac{1}{2}\delta s x\sqrt{3}$ and use the identity

$$\int_0^\infty \Big(\frac{\sin y}{y}\Big)^2 dy = \frac{\pi}{2}. \qquad \text{(B-12)}$$

Combining Eqs. (B-10) and (B-11), we conclude that R_1 is of order of δ^2. Neglecting terms beyond the first order of smallness with respect to δ, we find from Eqs. (B-4) and (B-9) that

$$C_1 = \frac{2\delta}{3} \int_0^\infty a(x)dx. \qquad \text{(B-13)}$$

Integration by parts with the help of Eqs. (A-8) and (B-12) results in

$$\int_0^\infty a(x)dx = \frac{\pi}{4}. \qquad \text{(B-14)}$$

Equations (B-13) and (B-14) result in Eq. (26).

Equation (28) follows from Eq. (27) and the identity

$$\int_0^\infty \exp\Big(-\frac{3\tilde{Q}^2}{2}\Big)\tilde{Q}^4 d\tilde{Q} = \frac{1}{3}\sqrt{\frac{\pi}{6}}. \qquad \text{(B-15)}$$

To determine the coefficient B_1, we substitute expression (A-8) into Eq. (29), set $x = \tilde{Q}/\delta$, change the order of integration, and find that

$$B_1 = 2\delta^5 \int_0^\infty a(z)dz \int_z^\infty \exp\Big(-\frac{3\delta^2 x^2}{2}\Big)x^3 dx.$$

Bearing in mind that

$$\int_z^\infty \exp\Big(-\frac{3\delta^2 x^2}{2}\Big)x^3 dx = \frac{1}{3\delta^2}\Big(z^2 + \frac{2}{3\delta^2}\Big)\exp\Big(-\frac{3\delta^2 z^2}{2}\Big), \qquad \text{(B-16)}$$

we obtain

$$B_1 = \frac{4}{9}\Big[\int_0^\infty a(\frac{y}{\delta})\exp\Big(-\frac{3y^2}{2}\Big)dy + \frac{3}{2}\int_0^\infty a(\frac{y}{\delta})\exp\Big(-\frac{3y^2}{2}\Big)y^2 dy\Big]. \qquad \text{(B-17)}$$

The first integral is given by Eq. (B-3). To determine the other integral, we use Eq. (B-5) for the function a and change the order of integration,

$$\int_0^\infty a(\frac{y}{\delta})\exp\Big(-\frac{3y^2}{2}\Big)y^2 dy = \frac{1}{4\pi}\int_{-\infty}^\infty \hat{a}(s)ds \int_{-\infty}^\infty \exp\Big[-\Big(\frac{3y^2}{2} + \frac{\imath s y}{\delta}\Big)\Big]y^2 dy. \qquad \text{(B-18)}$$

The internal integral in Eq. (B-18) is calculated explicitly

$$\int_{-\infty}^\infty \exp\Big[-\Big(\frac{3y^2}{2} + \frac{\imath s y}{\delta}\Big)\Big]y^2 dy = \frac{1}{3}\sqrt{\frac{2\pi}{3}}\exp\Big(-\frac{s^2}{6\delta^2}\Big)\Big(1 - \frac{s^2}{3\delta^2}\Big). \qquad \text{(B-19)}$$

Substitution of Eqs. (B-3), (B-18) and (B-19) into Eq. (B-17) results in

$$B_1 = \frac{2}{3}\Big[C_1 + \frac{\delta}{6\sqrt{2\pi}} \int_{-\infty}^{\infty} \hat{a}(\delta z\sqrt{3}) \exp\Big(-\frac{z^2}{2}\Big)(1-z^2)dz\Big], \tag{B-20}$$

where $z = s/(\delta\sqrt{3})$. Evaluating the integral by using the same approach that was applied to derive Eq. (B-13) and utilizing the identity

$$\int_{-\infty}^{\infty} \exp\Big(-\frac{z^2}{2}\Big)(1-z^2)dz = 0, \tag{B-21}$$

we find that the order of smallness of the second term on the right-hand side of Eq. (B-20) is higher than that of the first term. Equation (30) follows from Eqs. (B-13), (B-14) and (B-20).

Appendix C

Substitution of expressions (32) to (34) into Eq. (1) results in

$$H_0(\mathbf{r}) = \frac{3k_{\rm B}T}{2b_0}\Big[\frac{Q^2}{L} + \sum_{m,n=1}^{\infty} \frac{\pi m}{L}\frac{\pi n}{L}(X_m X_n + Y_m Y_n)\int_0^L \cos\frac{\pi m s}{L}\cos\frac{\pi n s}{L} ds\Big].$$

Employing the orthogonality of the trigonometric functions and Eq. (12), we arrive at

$$H_0(\mathbf{r}) = \frac{3k_{\rm B}T}{2b^2}\Big[Q^2 + \frac{\pi^2}{2}\sum_{m=1}^{\infty} m^2(X_m^2 + Y_m^2)\Big]. \tag{C-1}$$

The first equality in Eq. (35) follows from Eq. (C-1).

Substituting Eq. (32) into the exponent in Eq. (13), expanding the obtained expression into the Taylor series, and omitting terms beyond the second order of smallness with respect to $|\mathbf{R}|$, we find that

$$\begin{aligned}\exp\Big[-\imath\mathbf{k}\cdot\Big(\mathbf{r}(s)-\mathbf{r}(s')\Big)\Big] &= \exp\Big[-\imath\mathbf{k}\cdot\mathbf{Q}\frac{s-s'}{L}\Big]\Big\{1-\imath\mathbf{k}\cdot\Big(\mathbf{R}(s)-\mathbf{R}(s')\Big)\\ &\quad -\frac{1}{2}\Big[\mathbf{k}\cdot\Big(\mathbf{R}(s)-\mathbf{R}(s')\Big)\Big]^2\Big\}.\end{aligned} \tag{C-2}$$

Bearing in mind that $\mathbf{Q} = Q\mathbf{e}_3$, we conclude from Eq. (34) that

$$\mathbf{k}\cdot\mathbf{Q} = k_3 Q, \qquad \mathbf{k}\cdot\mathbf{R}(s) = \sum_{m=1}^{\infty}(k_1 X_m + k_2 Y_m)\sin\frac{\pi m s}{L}.$$

Substitution of these expressions into Eq. (C-2) results in

$$\begin{aligned}&\exp\Big[-\imath\mathbf{k}\cdot\Big(\mathbf{r}(s)-\mathbf{r}(s')\Big)\Big] = \exp\Big(-\imath k_3 Q\frac{s-s'}{L}\Big)\Big[1-\imath\sum_{m=1}^{\infty}(k_1X_m+k_2Y_m)\\ &\times\Big(\sin\frac{\pi m s}{L}-\sin\frac{\pi m s'}{L}\Big) - \frac{1}{2}\sum_{m,n=1}^{\infty}(k_1X_m+k_2Y_m)\Big(\sin\frac{\pi m s}{L}-\sin\frac{\pi m s'}{L}\Big)\\ &\times(k_1X_n+k_2Y_n)\Big(\sin\frac{\pi n s}{L}-\sin\frac{\pi n s'}{L}\Big)\Big].\end{aligned} \tag{C-3}$$

Combining Eq. (C-3) with Eqs. (13) and (14), we find that

$$\bar{V}(\mathbf{r}) = \bar{V}(\mathbf{r}_0) + \frac{v_0}{2L^2(2\pi)^3}\Big[\bar{V}_1(\mathbf{R}) + \bar{V}_2(\mathbf{R})\Big], \tag{C-4}$$

where

$$\bar{V}_1 = \int U(\mathbf{k})P_1(\mathbf{k})d\mathbf{k}, \qquad \bar{V}_2 = \int U(\mathbf{k})P_2(\mathbf{k})d\mathbf{k}. \tag{C-5}$$

The functions P_1 and P_2 in Eq. (C-5) are given by

$$\begin{aligned} P_1(\mathbf{k}) &= -\frac{\imath}{2}\sum_{m=1}^{\infty}(k_1X_m + k_2Y_m)p_m(k_3Q), \\ P_2(\mathbf{k}) &= -\frac{1}{2}\sum_{m,n=1}^{\infty}(k_1X_m + k_2Y_m)(k_1X_n + k_2Y_n)p_{mn}(k_3Q), \end{aligned} \tag{C-6}$$

where the coefficients p_m and p_{mn} read

$$\begin{aligned} p_m(k_3Q) &= \int_0^L ds\int_0^L \exp\Big(-\imath k_3Q\frac{s-s'}{L}\Big)\Big(\sin\frac{\pi ms}{L} - \sin\frac{\pi ms'}{L}\Big)ds', \\ p_{mn}(k_3Q) &= \int_0^L ds\int_0^L \exp\Big(-\imath k_3Q\frac{s-s'}{L}\Big)\Big(\sin\frac{\pi ms}{L} - \sin\frac{\pi ms'}{L}\Big)\Big(\sin\frac{\pi ns}{L} - \sin\frac{\pi ns'}{L}\Big)ds'. \end{aligned} \tag{C-7}$$

In spherical coordinates $\{k,\phi,\theta\}$, the Cartesian components of the vector $\mathbf{k}$ read

$$k_1 = k\sin\theta\cos\phi, \quad k_2 = k\sin\theta\sin\phi, \quad k_3 = k\cos\theta.$$

Substitution of these relations into Eqs. (C-5) and (C-6) implies that

$$\bar{V}_1 = -\frac{\imath}{2}\sum_{m=1}^{\infty}\int_0^{\infty}U_*(k)k^3dk\int_0^{2\pi}\Big(X_m\cos\phi + Y_m\sin\phi\Big)d\phi\int_0^{\pi}p_m(kQ\cos\theta)\sin^2\theta d\theta = 0. \tag{C-8}$$

By analogy with Eq. (C-8), we write

$$\begin{aligned} \bar{V}_2 &= -\frac{1}{2}\sum_{m,n=1}^{\infty}\int_0^{\infty}U_*(k)k^4dk\int_0^{2\pi}\Big[X_mX_n\cos^2\phi \\ &\quad +(X_mY_n + X_nY_m)\sin\phi\cos\phi + Y_mY_n\sin^2\phi\Big]d\phi\int_0^{\pi}p_{mn}(kQ\cos\theta)\sin^3\theta d\theta. \end{aligned}$$

Calculating the integral over ϕ and introducing the new variable $x=\cos\theta$, we arrive at

$$\bar{V}_2 = -\frac{\pi}{2}\sum_{m,n=1}^{\infty}(X_mX_n + Y_mY_n)\int_0^{\infty}U_*(k)k^4dk\int_{-1}^{1}p_{mn}(kQx)(1-x^2)dx. \tag{C-9}$$

Substitution of expressions (C-8) and (C-9) into Eq. (C-4) implies that

$$\bar{V}(\mathbf{r}) = \bar{V}(\mathbf{r}_0) - \frac{v_0}{32\pi^2L^2}\sum_{m,n=1}^{\infty}(X_mX_n + Y_mY_n)\int_0^{\infty}U_*(k)k^4dk\int_{-1}^{1}p_{mn}(kQx)(1-x^2)dx. \tag{C-10}$$

Our aim now is to determine the coefficients p_{mn}. It follows from Eq. (C-7) that

$$p_{mn} = p_{mn}^{(1)} - p_{mn}^{(2)} - p_{nm}^{(2)} + p_{mn}^{(3)}, \tag{C-11}$$

where

$$\begin{aligned}
p^{(1)}_{mn} &= \int_0^L \exp\Big(-\imath k_3 Q \frac{s}{L}\Big) \sin\frac{\pi m s}{L} \sin\frac{\pi n s}{L} ds \int_0^L \exp\Big(\imath k_3 Q \frac{s'}{L}\Big) ds', \\
p^{(2)}_{mn} &= \int_0^L \exp\Big(-\imath k_3 Q \frac{s}{L}\Big) \sin\frac{\pi n s}{L} ds \int_0^L \exp\Big(\imath k_3 Q \frac{s'}{L}\Big) \sin\frac{\pi m s'}{L} ds', \\
p^{(3)}_{mn} &= \int_0^L \exp\Big(-\imath k_3 Q \frac{s}{L}\Big) ds \int_0^L \exp\Big(\imath k_3 Q \frac{s'}{L}\Big) \sin\frac{\pi m s'}{L} \sin\frac{\pi n s'}{L} ds'.
\end{aligned} \tag{C-12}$$

We begin with the quantity

$$B_{mn} = \int_0^L \exp\Big(-\imath k_3 Q \frac{s}{L}\Big) \sin\frac{\pi m s}{L} \sin\frac{\pi n s}{L} ds = \frac{1}{2}(B^{(1)}_{mn} - B^{(2)}_{mn}), \tag{C-13}$$

where

$$\begin{aligned}
B^{(1)}_{mn} &= \int_0^L \exp\Big(-\imath k_3 Q \frac{s}{L}\Big) \cos\frac{\pi(m-n)s}{L} ds, \\
B^{(2)}_{mn} &= \int_0^L \exp\Big(-\imath k_3 Q \frac{s}{L}\Big) \cos\frac{\pi(m+n)s}{L} ds.
\end{aligned} \tag{C-14}$$

Using the formula $\cos\frac{\pi l s}{L} = \frac{1}{2}\Big[\exp\Big(\frac{\imath\pi l s}{L}\Big) + \exp\Big(-\frac{\imath\pi l s}{L}\Big)\Big]$ and calculating the integral in Eq. (C-14), we obtain

$$\begin{aligned}
B^{(1)}_{mn} &= \frac{1}{2}\int_0^L \Big[\exp\Big(-\imath(k_3 Q - \pi(m-n))\frac{s}{L}\Big) + \exp\Big(-\imath(k_3 Q + \pi(m-n))\frac{s}{L}\Big)\Big] ds \\
&= -\frac{L}{2\imath}\Big[\frac{1}{k_3 Q - \pi(m-n)}\Big(\exp\Big(-\imath(k_3 Q - \pi(m-n))\Big) - 1\Big) \\
&\quad + \frac{1}{k_3 Q + \pi(m-n)}\Big(\exp\Big(-\imath(k_3 Q + \pi(m-n))\Big) - 1\Big)\Big].
\end{aligned}$$

Taking into account that

$$\exp(-\imath x) - 1 = -2\imath \sin\frac{x}{2} \exp(-\frac{\imath x}{2}), \tag{C-15}$$

we find that

$$\begin{aligned}
B^{(1)}_{mn} &= L \exp\Big(-\frac{\imath}{2} k_3 Q\Big) \Big[\exp\Big(\frac{\pi}{2}\imath(m-n)\Big) F(k_3 Q - \pi(m-n)) \\
&\quad + \exp\Big(-\frac{\pi}{2}\imath(m-n)\Big) F(k_3 Q + \pi(m-n))\Big],
\end{aligned}$$

where the function $F(z)$ is determined by Eq. (37). Similar transformations result in

$$\begin{aligned}
B^{(2)}_{mn} &= L \exp\Big(-\frac{\imath}{2} k_3 Q\Big) \Big[\exp\Big(\frac{\pi}{2}\imath(m+n)\Big) F(k_3 Q - \pi(m+n)) \\
&\quad + \exp\Big(-\frac{\pi}{2}\imath(m+n)\Big) F(k_3 Q + \pi(m+n))\Big].
\end{aligned}$$

Substitution of these expressions into Eq. (C-13) implies that

$$\begin{aligned}
B_{mn} &= \frac{L}{2} \exp\Big(-\frac{\imath}{2} k_3 Q\Big) \Big\{\Big[\exp\Big(\frac{\pi}{2}\imath(m-n)\Big) F(k_3 Q - \pi(m-n)) \\
&\quad + \exp\Big(-\frac{\pi}{2}\imath(m-n)\Big) F(k_3 Q + \pi(m-n))\Big] \\
&\quad - \Big[\exp\Big(\frac{\pi}{2}\imath(m+n)\Big) F(k_3 Q - \pi(m+n)) \\
&\quad + \exp\Big(-\frac{\pi}{2}\imath(m+n)\Big) F(k_3 Q + \pi(m+n))\Big]\Big\}.
\end{aligned} \tag{C-16}$$

It follows from Eqs. (37), (A-3) and (C-15) that

$$\int_0^L \exp\Big(\imath k_3 Q \frac{s'}{L}\Big) ds' = 2L \exp(\frac{\imath}{2} k_3 Q) F(k_3 Q). \tag{C-17}$$

Substitution of Eqs. (C-16) and (C-17) into Eq. (C-12) results in

$$\begin{aligned} p_{mn}^{(1)} &= L^2 F(k_3 Q)\Big\{\Big[\exp\Big(\frac{\pi}{2}\imath(m-n)\Big) F(k_3 Q - \pi(m-n)) \\ &\quad + \exp\Big(-\frac{\pi}{2}\imath(m-n)\Big) F(k_3 Q + \pi(m-n))\Big] \\ &\quad - \Big[\exp\Big(\frac{\pi}{2}\imath(m+n)\Big) F(k_3 Q - \pi(m+n)) \\ &\quad + \exp\Big(-\frac{\pi}{2}\imath(m+n)\Big) F(k_3 Q + \pi(m+n))\Big]\Big\}. \end{aligned}$$

Replacing the exponents by trigonometric functions, we find that

$$\begin{aligned} p_{mn}^{(1)} &= L^2 F(k_3 Q)\Big\langle \Big\{\cos\frac{\pi(m-n)}{2}\Big[F(k_3 Q + \pi(m-n)) + F(k_3 Q - \pi(m-n))\Big] \\ &\quad - \cos\frac{\pi(m+n)}{2}\Big[F(k_3 Q + \pi(m+n)) + F(k_3 Q - \pi(m+n))\Big]\Big\} \\ &\quad + \imath\Big\{-\sin\frac{\pi(m-n)}{2}\Big[F(k_3 Q + \pi(m-n)) - F(k_3 Q - \pi(m-n))\Big] \\ &\quad + \sin\frac{\pi(m+n)}{2}\Big[F(k_3 Q + \pi(m+n)) - F(k_3 Q - \pi(m+n))\Big]\Big\}\Big\rangle. \end{aligned} \tag{C-18}$$

We proceed with transformation of the quantity

$$C_{mn} = \int_0^L \exp\Big(\imath k_3 Q \frac{s'}{L}\Big) \sin\frac{\pi m s'}{L} \sin\frac{\pi n s'}{L} ds'. \tag{C-19}$$

Comparison of expressions (C-13) and (C-19) implies that $C_{mn}(k_3)$ coincides with $B_{mn}(-k_3)$. According to Eq. (C-16), this means that

$$\begin{aligned} C_{mn} &= \frac{L}{2}\exp\Big(\frac{\imath}{2} k_3 Q\Big)\Big\{\Big[\exp\Big(\frac{\pi}{2}\imath(m-n)\Big) F(-k_3 Q - \pi(m-n)) \\ &\quad + \exp\Big(-\frac{\pi}{2}\imath(m-n)\Big) F(-k_3 Q + \pi(m-n))\Big] \\ &\quad - \Big[\exp\Big(\frac{\pi}{2}\imath(m+n)\Big) F(-k_3 Q - \pi(m+n)) \\ &\quad + \exp\Big(-\frac{\pi}{2}\imath(m+n)\Big) F(-k_3 Q + \pi(m+n))\Big]\Big\}. \end{aligned}$$

Bearing in mind that the function $F(z)$ is even, we find that

$$\begin{aligned} C_{mn} &= \frac{L}{2}\exp\Big(\frac{\imath}{2} k_3 Q\Big)\Big\{\Big[\exp\Big(\frac{\pi}{2}\imath(m-n)\Big) F(k_3 Q + \pi(m-n)) \\ &\quad + \exp\Big(-\frac{\pi}{2}\imath(m-n)\Big) F(k_3 Q - \pi(m-n))\Big] \\ &\quad - \Big[\exp\Big(\frac{\pi}{2}\imath(m+n)\Big) F(k_3 Q + \pi(m+n)) \\ &\quad + \exp\Big(-\frac{\pi}{2}\imath(m+n)\Big) F(k_3 Q - \pi(m+n))\Big]\Big\}. \end{aligned} \tag{C-20}$$

It follows from Eq. (C-17) that

$$\int_0^L \exp\Bigl(-\imath k_3 Q \frac{s}{L}\Bigr) ds = 2L \exp(-\frac{\imath}{2} k_3 Q) F(k_3 Q). \tag{C-21}$$

Substitution of expressions (C-20) and (C-21) into Eq. (C-12) results in

$$\begin{aligned} p_{mn}^{(3)} &= L^2 F(k_3 Q)\Bigl\{\Bigl[\exp\Bigl(\frac{\pi}{2}\imath(m-n)\Bigr) F(k_3 Q + \pi(m-n)) \\ &\quad + \exp\Bigl(-\frac{\pi}{2}\imath(m-n)\Bigr) F(k_3 Q - \pi(m-n))\Bigr] \\ &\quad - \Bigl[\exp\Bigl(\frac{\pi}{2}\imath(m+n)\Bigr) F(k_3 Q + \pi(m+n)) \\ &\quad + \exp\Bigl(-\frac{\pi}{2}\imath(m+n)\Bigr) F(k_3 Q - \pi(m+n))\Bigr]\Bigr\}. \end{aligned}$$

In the trigonometric form, this equality reads

$$\begin{aligned} p_{mn}^{(3)} &= L^2 F(k_3 Q)\Bigl\langle\Bigl\{\cos\frac{\pi(m-n)}{2}\Bigl[F(k_3 Q + \pi(m-n)) + F(k_3 Q - \pi(m-n))\Bigr] \\ &\quad - \cos\frac{\pi(m+n)}{2}\Bigl[F(k_3 Q + \pi(m+n)) + F(k_3 Q - \pi(m+n))\Bigr]\Bigr\} \\ &\quad + \imath\Bigl\{\sin\frac{\pi(m-n)}{2}\Bigl[F(k_3 Q + \pi(m-n)) - F(k_3 Q - \pi(m-n))\Bigr] \\ &\quad - \sin\frac{\pi(m+n)}{2}\Bigl[F(k_3 Q + \pi(m+n)) - F(k_3 Q - \pi(m+n))\Bigr]\Bigr\}\Bigr\rangle. \end{aligned} \tag{C-22}$$

Combining Eqs. (C-18) and (C-22), we find that

$$\begin{aligned} p_{mn}^{(1)} + p_{mn}^{(3)} &= L^2 F(k_3 Q)\Bigl\{\cos\frac{\pi(m-n)}{2}\Bigl[F(k_3 Q + \pi(m-n)) + F(k_3 Q - \pi(m-n))\Bigr] \\ &\quad - \cos\frac{\pi(m+n)}{2}\Bigl[F(k_3 Q + \pi(m+n)) + F(k_3 Q - \pi(m+n))\Bigr]\Bigr\}. \end{aligned} \tag{C-23}$$

We now calculate the integrals

$$D_m^{\pm} = \int_0^L \exp\Bigl(\pm\imath k_3 Q \frac{s}{L}\Bigr) \sin\frac{\pi m s}{L} ds. \tag{C-24}$$

Bearing in mind that $\sin\frac{\pi m s}{L} = \frac{1}{2\imath}\Bigl[\exp\Bigl(\frac{\imath\pi m s}{L}\Bigr) - \exp\Bigl(-\frac{\imath\pi m s}{L}\Bigr)\Bigr]$, we find that

$$\begin{aligned} D_m^{+} &= \frac{1}{2\imath}\Bigl[\int_0^L \exp\Bigl(\imath(k_3 Q + \pi m)\frac{s}{L}\Bigr) ds - \int_0^L \exp\Bigl(\imath(k_3 Q - \pi m)\frac{s}{L}\Bigr) ds\Bigr] \\ &= \frac{L}{2}\Bigl[\frac{1}{k_3 Q - \pi m}\Bigl(\exp(\imath(k_3 Q - \pi m)) - 1\Bigr) \\ &\quad - \frac{1}{k_3 Q + \pi m}\Bigl(\exp(\imath(k_3 Q + \pi m)) - 1\Bigr)\Bigr]. \end{aligned}$$

It follows from this equality and Eq. (C-15) that

$$D_m^{+} = L\imath \exp\Bigl(\frac{\imath}{2} k_3 Q\Bigr)\Bigl[\exp\Bigl(-\frac{\pi}{2}\imath m\Bigr) F(k_3 Q - \pi m) - \exp\Bigl(\frac{\pi}{2}\imath m\Bigr) F(k_3 Q + \pi m)\Bigr].$$

Similarly, we find that

$$D_m^- = L\imath \exp\Big(-\frac{\imath}{2}k_3Q\Big)\Big[\exp\Big(-\frac{\pi}{2}\imath m\Big)F(k_3Q+\pi m)-\exp\Big(\frac{\pi}{2}\imath m\Big)F(k_3Q-\pi m)\Big].$$

Substitution of these expressions into Eq. (C-12) implies that

$$\begin{aligned} p_{mn}^{(2)} &= L^2\Big[\exp\Big(\frac{\pi}{2}\imath m\Big)F(k_3Q+\pi m)-\exp\Big(-\frac{\pi}{2}\imath m\Big)F(k_3Q-\pi m)\Big] \\ &\quad\times\Big[\exp\Big(-\frac{\pi}{2}\imath n\Big)F(k_3Q+\pi n)-\exp\Big(\frac{\pi}{2}\imath n\Big)F(k_3Q-\pi n)\Big]. \end{aligned}$$

Taking into account that $\exp\Big(\frac{\pi}{2}\imath n\Big)=\cos\frac{\pi n}{2}+\imath\sin\frac{\pi n}{2}$, we arrive at the formula

$$\begin{aligned} p_{mn}^{(2)} &= L^2\Big[\cos\frac{\pi m}{2}\Big(F(k_3Q+\pi m)-F(k_3Q-\pi m)\Big) \\ &\quad+\imath\sin\frac{\pi m}{2}\Big(F(k_3Q+\pi m)+F(k_3Q-\pi m)\Big)\Big] \\ &\quad\times\Big[\cos\frac{\pi n}{2}\Big(F(k_3Q+\pi n)-F(k_3Q-\pi n)\Big) \\ &\quad-\imath\sin\frac{\pi n}{2}\Big(F(k_3Q+\pi n)+F(k_3Q-\pi n)\Big)\Big]. \end{aligned}$$

It follows from this equality that

$$p_{mn}^{(2)} = L^2(r_{mn}+\imath s_{mn}), \tag{C-25}$$

where

$$\begin{aligned} r_{mn} &= \cos\frac{\pi m}{2}\cos\frac{\pi n}{2}\Big[F(k_3Q+\pi m)-F(k_3Q-\pi m)\Big]\Big[F(k_3Q+\pi n)-F(k_3Q-\pi n)\Big] \\ &\quad+\sin\frac{\pi m}{2}\sin\frac{\pi n}{2}\Big[F(k_3Q+\pi m)+F(k_3Q-\pi m)\Big]\Big[F(k_3Q+\pi n)+F(k_3Q-\pi n)\Big], \\ s_{mn} &= \sin\frac{\pi m}{2}\cos\frac{\pi n}{2}\Big[F(k_3Q+\pi m)+F(k_3Q-\pi m)\Big]\Big[F(k_3Q+\pi n)-F(k_3Q-\pi n)\Big] \\ &\quad-\cos\frac{\pi m}{2}\sin\frac{\pi n}{2}\Big[F(k_3Q+\pi m)-F(k_3Q-\pi m)\Big]\Big[F(k_3Q+\pi n)+F(k_3Q-\pi n)\Big]. \end{aligned}$$

As $r_{nm}=r_{mn}$ and $s_{nm}=-s_{mn}$, we find from Eq. (C-25) that

$$\begin{aligned} p_{mn}^{(2)}+p_{nm}^{(2)} &= 2L^2\Big\{\cos\frac{\pi m}{2}\cos\frac{\pi n}{2}\Big[F(k_3Q+\pi m)-F(k_3Q-\pi m)\Big] \\ &\quad\times\Big[F(k_3Q+\pi n)-F(k_3Q-\pi n)\Big] \\ &\quad+\sin\frac{\pi m}{2}\sin\frac{\pi n}{2}\Big[F(k_3Q+\pi m)+F(k_3Q-\pi m)\Big] \\ &\quad\times\Big[F(k_3Q+\pi n)+F(k_3Q-\pi n)\Big]\Big\}. \end{aligned} \tag{C-26}$$

Substitution of expressions (C-23) and (C-26) into Eq. (C-11) results in

$$\begin{aligned} p_{mn} &= 2L^2\Big\{F(k_3Q)\Big[\cos\frac{\pi(m-n)}{2}\Big(F(k_3Q+\pi(m-n))+F(k_3Q-\pi(m-n))\Big) \\ &\quad-\cos\frac{\pi(m+n)}{2}\Big(F(k_3Q+\pi(m+n))+F(k_3Q-\pi(m+n))\Big)\Big] \\ &\quad-\cos\frac{\pi m}{2}\cos\frac{\pi n}{2}\Big[F(k_3Q+\pi m)-F(k_3Q-\pi m)\Big] \\ &\quad\times\Big[F(k_3Q+\pi n)-F(k_3Q-\pi n)\Big]-\sin\frac{\pi m}{2}\sin\frac{\pi n}{2}\Big[F(k_3Q+\pi m) \\ &\quad+F(k_3Q-\pi m)\Big]\Big[F(k_3Q+\pi n)+F(k_3Q-\pi n)\Big]\Big\}. \end{aligned} \tag{C-27}$$

It follows from Eqs. (C-10) and (C-27) that the potential $\bar{V}(\mathbf{r})$ is given by Eq. (35), where the coefficients

$$P_{mn} = \frac{1}{2L^2}\int_0^\infty U_*(k)k^4 dk \int_{-1}^1 p_{mn}(kQx)(1-x^2)dx \tag{C-28}$$

are determined by Eq. (36).

Setting $n=m$ in Eq. (C-27), we find that

$$\begin{aligned} p_{mm} &= 2L^2\Big\{F(k_3Q)\Big[2F(k_3Q)-\cos(\pi m)\Big(F(k_3Q+2\pi m)+F(k_3Q-2\pi m)\Big)\Big] \\ &- \cos^2\frac{\pi m}{2}\Big[F(k_3Q+\pi m)-F(k_3Q-\pi m)\Big]^2 - \sin^2\frac{\pi m}{2}\Big[F(k_3Q+\pi m) \\ &+F(k_3Q-\pi m)\Big]^2\Big\}. \end{aligned}$$

Bearing in mind that

$$\begin{aligned} &\sin^2\frac{\pi m}{2}\Big(F(k_3Q+\pi m)+F(k_3Q-\pi m)\Big)^2+\cos^2\frac{\pi m}{2}\Big(F(k_3Q+\pi m)-F(k_3Q-\pi m)\Big)^2 \\ &= F^2(k_3Q+\pi m)+F^2(k_3Q-\pi m)-2\cos(\pi m)F(k_3Q+\pi m)F(k_3Q-\pi m), \end{aligned}$$

we arrive at the formula

$$\begin{aligned} p_{mm} &= 2L^2\Big\{\Big[2F^2(k_3Q)-F^2(k_3Q+\pi m)-F^2(k_3Q-\pi m)\Big] \\ &-\cos(\pi m)\Big[F(k_3Q)\Big(F(k_3Q+2\pi m)+F(k_3Q-2\pi m)\Big) \\ &-2F(k_3Q+\pi m)F(k_3Q-\pi m)\Big]\Big\}. \end{aligned} \tag{C-29}$$

Appendix D

It follows from Eqs. (43), (C-28) and (C-29) that

$$\begin{aligned} S &= \int_0^\infty U_*(k)k^4 dk\int_{-1}^1(1-x^2)dx\Big\{\sum_{m=1}^\infty\frac{1}{m^2}\Big[F^2(kQx+\pi m)+F^2(kQx-\pi m)\Big] \\ &+F(kQx)\sum_{m=1}^\infty\frac{(-1)^m}{m^2}\Big[F(kQx+2\pi m)+F(kQx-2\pi m)\Big] \\ &+2\sum_{m=1}^\infty\frac{(-1)^m}{m^2}F(kQx+\pi m)F(kQx-\pi m)-2F^2(kQx)\sum_{m=1}^\infty\frac{1}{m^2}\Big\}. \end{aligned}$$

Bearing in mind that

$$\sum_{m=1}^\infty\frac{1}{m^2}=\frac{\pi^2}{6}, \tag{D-1}$$

we arrive at Eqs. (44) and (45).

We begin with calculation of $s_1(z)$. It follows from Eq. (37) that

$$F(z+2\pi m)+F(z-2\pi m)=\frac{1}{z+2\pi m}\sin\Big(\frac{z}{2}+\pi m\Big)+\frac{1}{z-2\pi m}\sin\Big(\frac{z}{2}-\pi m\Big).$$

Taking into account that for any integer m,

$$\sin\Big(\frac{z}{2}\pm\pi m\Big)=(-1)^m\sin\frac{z}{2},$$

we obtain

$$F(z+2\pi m)+F(z-2\pi m)=(-1)^m\sin\frac{z}{2}\Big(\frac{1}{z+2\pi m}+\frac{1}{z-2\pi m}\Big)=2\frac{(-1)^m z}{z^2-(2\pi m)^2}\sin\frac{z}{2}.$$

This equality together with Eq. (45) implies that

$$s_1(z)=2z\sin\frac{z}{2}\sum_{m=1}^{\infty}\frac{1}{m^2(z^2-(2\pi m)^2)}.$$

It follows from the identity

$$\frac{1}{m^2(z^2-(2\pi m)^2)}=\frac{1}{z^2}\Big[\frac{1}{m^2}+\frac{(2\pi)^2}{z^2-(2\pi m)^2}\Big]$$

that

$$s_1(z)=\frac{2}{z}\sin\frac{z}{2}\Big[\sum_{m=1}^{\infty}\frac{1}{m^2}+(2\pi)^2\sum_{m=1}^{\infty}\frac{1}{z^2-(2\pi m)^2}\Big].$$

Using Eqs. (37) and (D-1), we transform this equality as follows:

$$s_1(z)=2\pi^2F(z)\Big[\frac{1}{6}+4\sum_{m=1}^{\infty}\frac{1}{z^2-(2\pi m)^2}\Big]. \tag{D-2}$$

Setting $z=2z_1$, we obtain

$$4\sum_{m=1}^{\infty}\frac{1}{z^2-(2\pi m)^2}=\sum_{m=1}^{\infty}\frac{1}{z_1^2-(\pi m)^2}.$$

The latter sum is well-known [47],

$$\sum_{m=1}^{\infty}\frac{1}{z^2-(\pi m)^2}=\frac{1}{2z}\Big(\cot z-\frac{1}{z}\Big). \tag{D-3}$$

Substituting expression (D-3) into Eq. (D-2) and returning to the initial notation, we arrive at the formula

$$s_1(z)=2\pi^2F(z)\Big[\frac{1}{6}+\frac{1}{z}\Big(\cot\frac{z}{2}-\frac{2}{z}\Big)\Big]. \tag{D-4}$$

It follows from Eqs. (37) and (45) that the function $s_2(z)$ reads

$$s_2(z)=\sum_{m=1}^{\infty}\frac{1}{m^2}\Big[\frac{\sin^2(\frac{z}{2}+\frac{\pi m}{2})}{(z+\pi m)^2}+\frac{\sin^2(\frac{z}{2}-\frac{\pi m}{2})}{(z-\pi m)^2}\Big]=s_2^{(1)}(z)-s_2^{(2)}(z)\cos z, \tag{D-5}$$

where

$$s_2^{(1)}(z)=\sum_{m=1}^{\infty}\frac{z^2+(\pi m)^2}{m^2(z^2-(\pi m)^2)^2},\qquad s_2^{(2)}(z)=\sum_{m=1}^{\infty}\frac{(-1)^m(z^2+(\pi m)^2)}{m^2(z^2-(\pi m)^2)^2}. \tag{D-6}$$

To determine the function $s_2^{(1)}(z)$, we present the first equality in Eq. (D-6) in the form

$$s_2^{(1)}(z)=z^2\sum_{m=1}^{\infty}\frac{1}{m^2(z^2-(\pi m)^2)^2}+\pi^2\sum_{m=1}^{\infty}\frac{1}{(z^2-(\pi m)^2)^2}. \tag{D-7}$$

The first sum in Eq. (D-7) is transformed with the help of the identity

$$\frac{1}{m^2(z^2-(\pi m)^2)^2}=\frac{1}{z^4}\Big[\frac{1}{m^2}+\frac{\pi^2}{z^2-(\pi m)^2}+\frac{\pi^2 z^2}{(z^2-(\pi m)^2)^2}\Big]. \tag{D-8}$$

Combining Eqs. (D-7) and (D-8), we obtain

$$s_2^{(1)}(z)=\frac{1}{z^2}\sum_{m=1}^{\infty}\frac{1}{m^2}+\frac{\pi^2}{z^2}\sum_{m=1}^{\infty}\frac{1}{z^2-(\pi m)^2}+2\pi^2\sum_{m=1}^{\infty}\frac{1}{(z^2-(\pi m)^2)^2}. \tag{D-9}$$

Differentiation of Eq. (D-3) with respect to z implies that

$$\sum_{m=1}^{\infty}\frac{1}{(z^2-(\pi m)^2)^2}=\frac{1}{4z^2}\Big(\frac{\cot z}{z}+\frac{1}{\sin^2 z}-\frac{2}{z^2}\Big). \tag{D-10}$$

Substitution of expressions (D-1), (D-3) and (D-10) into Eq. (D-9) implies that

$$s_2^{(1)}(z)=\frac{\pi^2}{2z^2}\Big(\frac{1}{3}+2\frac{\cot z}{z}+\frac{1}{\sin^2 z}-\frac{3}{z^2}\Big). \tag{D-11}$$

According to Eq. (D-6), the function $s_2^{(2)}(z)$ is given by

$$s_2^{(2)}(z)=z^2\sum_{m=1}^{\infty}\frac{(-1)^m}{m^2(z^2-(\pi m)^2)^2}+\pi^2\sum_{m=1}^{\infty}\frac{(-1)^m}{(z^2-(\pi m)^2)^2}.$$

Combining this equality with Eq. (D-8), we find that

$$s_2^{(2)}(z)=\frac{1}{z^2}\sum_{m=1}^{\infty}\frac{(-1)^m}{m^2}+\frac{\pi^2}{z^2}\sum_{m=1}^{\infty}\frac{(-1)^m}{z^2-(\pi m)^2}+2\pi^2\sum_{m=1}^{\infty}\frac{(-1)^m}{(z^2-(\pi m)^2)^2}. \tag{D-12}$$

To evaluate the first sum in Eq. (D-12), we present Eq. (D-1) in the form

$$\frac{\pi^2}{6}=\sum_{m=1}^{\infty}\frac{1}{(2m-1)^2}+\sum_{m=1}^{\infty}\frac{1}{(2m)^2}=\sum_{m=1}^{\infty}\frac{1}{(2m-1)^2}+\frac{1}{4}\sum_{m=1}^{\infty}\frac{1}{m^2}.$$

Combination of this equality with Eq. (D-1) results in

$$\sum_{m=1}^{\infty}\frac{1}{(2m-1)^2}=\frac{\pi^2}{8},\qquad \sum_{m=1}^{\infty}\frac{1}{(2m)^2}=\frac{\pi^2}{24}. \tag{D-13}$$

Bearing in mind that

$$\sum_{m=1}^{\infty}\frac{(-1)^m}{m^2}=-\sum_{m=1}^{\infty}\frac{1}{(2m-1)^2}+\sum_{m=1}^{\infty}\frac{1}{(2m)^2},$$

we find from Eq. (D-13) that

$$\sum_{m=1}^{\infty}\frac{(-1)^m}{m^2}=-\frac{\pi^2}{12}. \tag{D-14}$$

The other sum in Eq. (D-12) is well-known [47],

$$\sum_{m=1}^{\infty}\frac{(-1)^m}{z^2-(\pi m)^2}=\frac{1}{2z}\Big(\frac{1}{\sin z}-\frac{1}{z}\Big). \tag{D-15}$$

Differentiation of Eq. (D-15) with respect to z results in

$$\sum_{m=1}^{\infty}\frac{(-1)^m}{(z^2-(\pi m)^2)^2}=\frac{1}{4z^2}\Big(\frac{1}{z\sin z}+\frac{\cos z}{\sin^2 z}-\frac{2}{z^2}\Big). \tag{D-16}$$

Substitution of expressions (D-14) to (D-16) into Eq. (D-12) implies that

$$s_2^{(2)}(z)=\frac{\pi^2}{2z^2}\Big(-\frac{1}{6}+\frac{2}{z\sin z}+\frac{\cos z}{\sin^2 z}-\frac{3}{z^2}\Big).$$

Combining this equality with Eqs. (D-5) and (D-11), we arrive at the formula

$$s_2(z)=\frac{\pi^2}{2z^2}\Big(\frac{8+\cos z}{6}-3\frac{1-\cos z}{z^2}\Big). \tag{D-17}$$

It follows from Eqs. (37) and (45) that

$$s_3(z)=\sum_{m=1}^{\infty}\frac{(-1)^m}{m^2}\frac{\sin(\frac{z}{2}+\frac{\pi m}{2})\sin(\frac{z}{2}-\frac{\pi m}{2})}{z^2-(\pi m)^2}.$$

Bearing in mind that

$$\sin(\frac{z}{2}+\frac{\pi m}{2})\sin(\frac{z}{2}-\frac{\pi m}{2})=\frac{1}{2}\Big(\cos(\pi m)-\cos z\Big)=\frac{1}{2}\Big[(-1)^m-\cos z\Big],$$

we find that

$$s_3(z)=\frac{1}{2}\Big[s_3^{(1)}(z)-s_3^{(2)}(z)\cos z\Big], \tag{D-18}$$

where

$$s_3^{(1)}(z)=\sum_{m=1}^{\infty}\frac{1}{m^2(z^2-(\pi m)^2)},\qquad s_3^{(2)}(z)=\sum_{m=1}^{\infty}\frac{(-1)^m}{m^2(z^2-(\pi m)^2)}.$$

Taking into account that

$$\frac{1}{m^2(z^2-(\pi m)^2)}=\frac{1}{z^2}\Big[\frac{1}{m^2}+\frac{\pi^2}{z^2-(\pi m)^2}\Big]$$

and employing Eqs. (D-1) and (D-3), we obtain

$$s_3^{(1)}(z)=\frac{\pi^2}{2z^2}\Big[\frac{1}{3}+\frac{1}{z}\Big(\cot z-\frac{1}{z}\Big)\Big]. \tag{D-19}$$

Similarly, we find that

$$s_3^{(2)}(z)=\frac{1}{z^2}\Big[\sum_{m=1}^{\infty}\frac{(-1)^m}{m^2}+\pi^2\sum_{m=1}^{\infty}\frac{(-1)^m}{z^2-(\pi m)^2}\Big]. \tag{D-20}$$

Substitution of expressions (D-14) and (D-15) into Eq. (D-20) implies that

$$s_3^{(2)}(z)=\frac{\pi^2}{2z^2}\Big[-\frac{1}{6}+\frac{1}{z}\Big(\frac{1}{\sin z}-\frac{1}{z}\Big)\Big].$$

Combining this equality with Eqs. (D-18) and (D-19), we find that

$$s_3(z)=\frac{\pi^2}{4z^2}\Big(\frac{2+\cos z}{6}-\frac{1-\cos z}{z^2}\Big). \tag{D-21}$$

Substitution of Eqs. (37), (D-4), (D-17) and (D-21) into Eq. (45) results in Eq. (46).

It follows from Eqs. (9) and (47) that

$$S = \frac{\pi^2}{b^2 \tilde{Q}^2} \int_0^1 \frac{1-x^2}{x^2} dx \int_0^{k_*} \alpha(kb\tilde{Q}x) k^2 dk.$$

Introducing the new variable $z = kb\tilde{Q}x$, we obtain

$$S = \frac{\pi^2}{b^5 \tilde{Q}^5} \int_0^1 \frac{1-x^2}{x^5} dx \int_0^{k_* b\tilde{Q}x} \alpha(z) z^2 dz.$$

We now set $y = k_* b\tilde{Q}x$ and change the order of integration,

$$\begin{aligned} S &= \frac{\pi^2 k_*^4}{b\tilde{Q}} \int_0^{k_* b\tilde{Q}} \Big(1 - \Big(\frac{y}{k_* b\tilde{Q}}\Big)^2\Big) \frac{dy}{y^5} \int_0^y \alpha(z) z^2 dz \\ &= \frac{\pi^2 k_*^4}{b\tilde{Q}} \int_0^{k_* b\tilde{Q}} \alpha(z) z^2 dz \int_z^{k_* b\tilde{Q}} \Big(1 - \Big(\frac{y}{k_* b\tilde{Q}}\Big)^2\Big) \frac{dy}{y^5}. \end{aligned} \tag{D-22}$$

Substituting the expression

$$\int_z^{k_* b\tilde{Q}} \Big(1 - \Big(\frac{y}{k_* b\tilde{Q}}\Big)^2\Big) \frac{dy}{y^5} = \frac{1}{4}\Big(\frac{1}{z^2} - \frac{1}{(k_* b\tilde{Q})^2}\Big)^2$$

into Eq. (D-22), we arrive at Eq. (48).

To transform expression (49) for the function $A_0(x)$, we, first, find from Eq. (46) that

$$\alpha(z) = 1 + 2z^2 \frac{d}{dz}\Big(\frac{1-\cos z}{z^3}\Big). \tag{D-23}$$

Substitution of Eq. (D-23) into Eq. (49) and integration by parts imply that

$$A_0(x) = \frac{1}{x^5}\Big[8 \int_0^x (x^2 - z^2) \frac{1-\cos z}{z^2} dz - 4 \int_0^x (x^2 - z^2) dz\Big].$$

Using Eq. (18) and calculating the second integral in this equality, we obtain

$$A_0(x) = \frac{8}{x^2}\Big[A(x) - \frac{1}{3}\Big]. \tag{D-24}$$

Using Eq. (D-24) and expanding the function $A(x)$ into the Taylor series in the vicinity of the point $x = 0$, we find that

$$\lim_{x\to 0} A_0(x) = 4 \frac{d^2 A}{dx^2}(0). \tag{D-25}$$

Differentiation of Eq. (A-8) with respect to x implies that

$$\frac{d^2 A}{dx^2}(x) = \frac{4}{x^3} \int_0^x \frac{z - \sin z}{z^3} dz + \frac{-8x + 10\sin x - 2x\cos x}{x^5}.$$

Applying L'Hospital's rule, we obtain

$$\frac{d^2 A}{dx^2}(0) = -\frac{1}{90}. \tag{D-26}$$

The first equality in Eq. (50) follows from Eqs. (D-25) and (D-26). The other equality is a consequence of Eqs. (19) and (D-24).

Appendix E

Substitution of expression (D-24) into Eq. (53) implies that

$$C_2 = 8\delta^2 \Big[\int_0^\infty A(\frac{x}{\delta}) \exp\Big(-\frac{3x^2}{2}\Big) dx - \frac{1}{6}\sqrt{\frac{2\pi}{3}} \Big]. \tag{E-1}$$

Our aim now is to prove that the first term in the square brackets

$$I = \int_0^\infty A(\frac{x}{\delta}) \exp\Big(-\frac{3x^2}{2}\Big) dx \tag{E-2}$$

is small compared with unity. It follows from Eq. (A-8) that for any y,

$$A(y) - \frac{2}{y}\int_0^\infty a(z)dz = -\frac{2}{y}\int_y^\infty a(z)dz. \tag{E-3}$$

Beaing in mind that

$$0 \leq a(z) = \frac{1}{z^2}\Big(1 - \frac{\sin z}{z}\Big) \leq \frac{2}{z^2},$$

we find from Eq. (E-3) that

$$\Big| A(y) - \frac{2}{y}\int_0^\infty a(z)dz \Big| \leq \frac{4}{y}\int_y^\infty \frac{dz}{z^2} = \frac{4}{y^2}. \tag{E-4}$$

Setting $y = x/\delta$ in Eq. (E-2), we obtain

$$I = \delta \int_0^\infty A(y) \exp\Big(-\frac{3\delta^2 y^2}{2}\Big) dy = \delta(I_1 + I_2 + I_3), \tag{E-5}$$

where

$$\begin{aligned} I_1 &= \int_0^1 A(y) \exp\Big(-\frac{3\delta^2 y^2}{2}\Big) dy, \\ I_2 &= \int_1^\infty \Big(A(y) - \frac{2}{y}\int_0^\infty a(z)dz\Big) \exp\Big(-\frac{3\delta^2 y^2}{2}\Big) dy, \\ I_3 &= 2\int_0^\infty a(z)dz \int_1^\infty \exp\Big(-\frac{3\delta^2 y^2}{2}\Big) \frac{dy}{y}. \end{aligned} \tag{E-6}$$

It follows from Eqs. (19) and (E-6) that

$$|I_1| \leq \int_0^1 A(y)dy \leq \frac{1}{3}. \tag{E-7}$$

Equations (E-4) and (E-6) imply that

$$|I_2| \leq 4\int_1^\infty \exp\Big(-\frac{3\delta^2 y^2}{2}\Big) \frac{dy}{y^2} \leq 4\int_1^\infty \frac{dy}{y^2} = 4. \tag{E-8}$$

According to Eqs. (B-14) and (E-6),

$$I_3 = \frac{\pi}{2}\int_1^\infty \exp\Big(-\frac{3\delta^2 y^2}{2}\Big) \frac{dy}{y} = \frac{\pi}{2}\int_\delta^\infty \exp\Big(-\frac{3x^2}{2}\Big) \frac{dx}{x},$$

where we return to the variable x. For $\delta < 1$, this equality reads

$$I_3 = \frac{\pi}{2}(I_3^{(1)} + I_3^{(2)}), \tag{E-9}$$

where

$$I_3^{(1)} = \int_\delta^1 \exp\Big(-\frac{3x^2}{2}\Big)\frac{dx}{x}, \qquad I_3^{(2)} = \int_1^\infty \exp\Big(-\frac{3x^2}{2}\Big)\frac{dx}{x}.$$

It follows from these equalities that

$$|I_3^{(1)}| \le \int_\delta^1 \frac{dx}{x} = -\ln\delta, \qquad |I_3^{(2)}| \le \int_1^\infty \exp\Big(-\frac{3x^2}{2}\Big)dx \le \int_0^\infty \exp\Big(-\frac{3x^2}{2}\Big)dx = \sqrt{\frac{\pi}{6}}. \tag{E-10}$$

Combining Eq. (E-5) with Eqs. (E-7) to (E-10), we arrive at the formula

$$|I| \le \delta\Big[\frac{13}{3} + \frac{\pi}{2}\Big(\sqrt{\frac{\pi}{6}} - \ln\delta\Big)\Big], \tag{E-11}$$

which completes the proof.

It follows from Eqs. (57) and (D-24) that

$$B_2 = 8\delta^2\Big[\int_0^\infty A(\frac{x}{\delta})\exp\Big(-\frac{3x^2}{2}\Big)x^2dx - \frac{1}{3}\int_0^\infty \exp\Big(-\frac{3x^2}{2}\Big)x^2dx\Big]. \tag{E-12}$$

According to Eq. (25), the first integral in Eq. (E-12) coincides with C_1. The other integral is given by Eq. (B-1). Substitution of these expressions into Eq. (E-12) results in

$$B_2 = 8\delta^2\Big(C_1 - \frac{1}{18}\sqrt{\frac{2\pi}{3}}\Big).$$

Combining this equality with Eq. (26) and disregarding terms beyond the second order of smallness, we arrive at Eq. (58).

Appendix F

To find Λ_1, we formally expand the denominator in the first equality in Eq. (64) into the Taylor series in $\mu_1 = -\mu$,

$$\frac{A_1(y)}{1 - \mu_1 A_1(y)} = A_1(y)\Big[1 + \mu_1 A_1(y) + \sum_{m=2}^\infty \Big(\mu_1 A_1(y)\Big)^m\Big], \tag{F-1}$$

and evaluate the integrals of appropriate terms in this sum. The integral

$$\Lambda_1^{(1)} = \int_0^\infty A_1(\frac{x}{\delta})\exp\Big(-\frac{3x^2}{2}\Big)x^2dx$$

was calculated previously. It follows from Eqs. (53), (54) and (62) that the leading term in the expression for $\Lambda_1^{(1)}$ is given by

$$\Lambda_1^{(1)} = \frac{2}{27}\sqrt{\frac{2\pi}{3}}\delta^2. \tag{F-2}$$

To find the coefficient

$$\Lambda_1^{(2)} = \int_0^\infty A_1^2(\frac{x}{\delta})\exp\Big(-\frac{3x^2}{2}\Big)x^2dx,$$

we substitute expressions (62) and (D-24) into this equality and obtain

$$\Lambda_1^{(2)} = \frac{2}{81}\delta^2 \int_0^\infty A_0(\frac{x}{\delta})\Big[A(\frac{x}{\delta}) - \frac{1}{3}\Big] \exp\Big(-\frac{3x^2}{2}\Big)dx. \tag{F-3}$$

The function

$$\alpha_1(x) = A_0(x)\Big[A(x) - \frac{1}{3}\Big]$$

is even and continuous, it has the zero limit at $x \to 0$ and vanishes being proportional to x^{-2} at $x \to \infty$. This means that the Fourier transform $\hat{\alpha}_1(s)$ of this function exists. Presenting Eq. (F-3) in the form

$$\Lambda_1^{(2)} = \frac{\delta^2}{162\pi} \int_{-\infty}^\infty \exp\Big(-\frac{3x^2}{2}\Big)dx \int_{-\infty}^\infty \hat{\alpha}_1(s) \exp\Big(-\frac{\imath sx}{\delta}\Big)ds$$

and evaluating the integral with the use of Eq. (B-7), we arrive at

$$\Lambda_1^{(2)} = \frac{\delta^3}{81\sqrt{2\pi}} \int_{-\infty}^\infty \hat{\alpha}_1(\delta z\sqrt{3}) \exp\Big(-\frac{z^2}{2}\Big)dz.$$

The leading term in this expression is obtained when the function $\hat{\alpha}_1(s)$ is expanded into the Taylor series in the vicinity of $s = 0$ and only the first term in the series is taken into account,

$$\Lambda_1^{(2)} = \frac{\delta^3}{81}\hat{\alpha}_1(0) = \frac{2\delta^3}{81} \int_0^\infty A_0(x)\Big[A(x) - \frac{1}{3}\Big]dx. \tag{F-4}$$

The integrals

$$\Lambda_1^{(m)} = \int_0^\infty A_1^m(\frac{x}{\delta}) \exp\Big(-\frac{3x^2}{2}\Big)x^2dx$$

with $m \geq 2$ are estimated by using a standard approach. Setting

$$\alpha_m(x) = A_1^m(x), \tag{F-5}$$

we re-write this equality in the form

$$\Lambda_1^{(m)} = \int_0^\infty \alpha_m(\frac{x}{\delta}) \exp\Big(-\frac{3x^2}{2}\Big)x^2dx. \tag{F-6}$$

It follows from Eqs. (62) and (D-24) that $A_1^m(x)$ vanishes at $x \to \infty$ being proportional to x^{-2m}. This means that for any $m \geq 2$, the second derivative with respect to s exists of the Fourier transform

$$\hat{\alpha}_m(s) = \int_{-\infty}^\infty \alpha_m(x) \exp(\imath sx)dx \tag{F-7}$$

of the function $\alpha_m(x)$. Bearing in mind that the function $\alpha_m(x)$ is even, substituting the expression

$$\alpha_m(\frac{x}{\delta}) = \frac{1}{2\pi} \int_{-\infty}^\infty \hat{\alpha}_m(s) \exp(-\frac{\imath sx}{\delta})ds$$

into Eq. (F-6) and changing the order of integration, we find that

$$\Lambda_1^{(m)} = \frac{1}{4\pi} \int_{-\infty}^\infty \hat{\alpha}_m(s)ds \int_{-\infty}^\infty \exp\Big[-\Big(\frac{3x^2}{2} + \frac{\imath sx}{\delta}\Big)\Big]x^2dx.$$

Using Eq. (B-19) for the internal integral and setting $z = s/(\delta\sqrt{3})$, we arrive at

$$\Lambda_1^{(m)} = \frac{\delta}{6\sqrt{2\pi}} \int_{-\infty}^{\infty} \hat{\alpha}_m(\delta z\sqrt{3}) \exp\Bigl(-\frac{z^2}{2}\Bigr)(1 - z^2) dz. \tag{F-8}$$

Expanding the even function $\hat{\alpha}_m(s)$ into the Taylor series in the vicinity of the point $s = 0$ and neglecting terms beyond the second order of smallness, we find that

$$\hat{\alpha}_m(\delta z\sqrt{3}) = \hat{\alpha}_m(0) + \frac{3\delta^2}{2} \frac{d^2\hat{\alpha}_m}{ds^2}(0) z^2.$$

We combine this equality with Eq. (F-8), use Eq. (B-21), and obtain

$$\Lambda_1^{(m)} = \frac{\delta^3}{4\sqrt{2\pi}} \frac{d^2\hat{\alpha}_m}{ds^2}(0) \int_{-\infty}^{\infty} \exp\Bigl(-\frac{z^2}{2}\Bigr)(1 - z^2) z^2 dz = -\frac{\delta^3}{2} \frac{d^2\hat{\alpha}_m}{ds^2}(0). \tag{F-9}$$

It follows from Eq. (F-7) that

$$\frac{d^2\hat{\alpha}_m}{ds^2}(0) = -2 \int_0^{\infty} \alpha_m(x) x^2 dx.$$

This equality together with Eqs. (F-5) and (F-9) yields

$$\Lambda_1^{(m)} = \delta^3 \int_0^{\infty} A_1^m(x) x^2 dx. \tag{F-10}$$

Substitution of expressions (F-1), (F-2), (F-4) and (F-10) into Eq. (64) results in

$$\Lambda_1 = \delta^2 \Bigl[\frac{2}{27}\sqrt{\frac{2\pi}{3}} + \frac{2}{81}\mu_1\delta \int_0^{\infty} A_0(x)\Bigl(A(x) - \frac{1}{3}\Bigr) dx + \frac{\delta}{\mu_1} \int_0^{\infty} \sum_{m=3}^{\infty} \mu_1^m A_1^m(x) x^2 dx \Bigr].$$

Taking into account that

$$\sum_{m=3}^{\infty} \Bigl(\mu_1 A_1(x)\Bigr)^m = \frac{\mu_1^3 A_1^3(x)}{1 - \mu_1 A_1(x)}, \tag{F-11}$$

and returning to the initial notation, we find that

$$\Lambda_1 = \delta^2 \Bigl[\frac{2}{27}\sqrt{\frac{2\pi}{3}} + \frac{4}{9}\mu\delta \int_0^{\infty} A_1(x)\Bigl(A(x) - \frac{1}{3}\Bigr) dx + \mu^2\delta \int_0^{\infty} \frac{A_1^3(x) x^2}{1 + \mu A_1(x)} dx \Bigr].$$

Combining the integral terms and utilizing Eqs. (62) and (D-24), we obtain

$$\Lambda_1 = \delta^2 \Bigl[\frac{2}{27}\sqrt{\frac{2\pi}{3}} - \mu\delta \int_0^{\infty} \frac{A_1^2(x) x^2}{1 + \mu A_1(x)} dx \Bigr]. \tag{F-12}$$

As all integrals in Eq. (F-12) converge, it can be shown that the above transformations are correct for an arbitrary (not necessary small) μ.

Equation (F-12) implies that the leading term in the expression for Λ_1 is (at least) of order of δ^2. As the quantity Λ_2 is included into Eq. (63) with the pre-factor δ^2, in order to disregard this term it suffices to show that Λ_2 is small compared with unity. Taking into account that the function $A_1(x)$ is non-negative, we write

$$\frac{A(x)}{1 + \mu A_1(x)} \le A(x). \tag{F-13}$$

This equality together with Eqs. (25) and (64) implies that

$$0 \le \Lambda_2 \le \int_0^\infty A(\frac{x}{\delta}) \exp\Big(-\frac{3x^2}{2}\Big) x^2 dx = C_1.$$

It follows from this inequality and Eq. (26) that the contribution of Λ_2 into Eq. (63) is negligible compared with Λ_1. This conclusion together with Eqs. (63) and (F-12) implies that

$$C = \Big(\frac{3}{2\pi b^2}\Big)^{\frac{3}{2}} \Big\{1 - \mu\delta^2 \Big[\frac{4}{9} - 6\sqrt{\frac{3}{2\pi}}\mu\delta \int_0^\infty \frac{A_1^2(x)x^2}{1+\mu A_1(x)} dx\Big]\Big\}^{-1}.$$

Equation (65) follows from this equality and Eq. (62).

To find the coefficient Γ_1, we evaluate the integrals of appropriate terms in expansion (F-1). The integral

$$\Gamma_1^{(1)} = \int_0^\infty A_1(\frac{x}{\delta}) \exp\Big(-\frac{3x^2}{2}\Big) x^4 dx$$

was calculated previously. It follows from Eqs. (57), (58) and (62) that the leading term in the expression for $\Gamma_1^{(1)}$ reads

$$\Gamma_1^{(1)} = \frac{2}{81}\sqrt{\frac{2\pi}{3}}\delta^2. \tag{F-14}$$

Using Eqs. (62) and (D-24), we transform the coefficient

$$\Gamma_1^{(2)} = \int_0^\infty A_1^2(\frac{x}{\delta}) \exp\Big(-\frac{3x^2}{2}\Big) x^4 dx$$

as follows:

$$\Gamma_1^{(2)} = \frac{16}{81}\delta^4 \Big[\int_0^\infty A^2(\frac{x}{\delta}) \exp\Big(-\frac{3x^2}{2}\Big) dx - \frac{2}{3}\int_0^\infty A(\frac{x}{\delta}) \exp\Big(-\frac{3x^2}{2}\Big) dx + \frac{1}{9}\int_0^\infty \exp\Big(-\frac{3x^2}{2}\Big) dx\Big].$$

The first term in the square brackets is of order of δ, because the Fourier transform of the function $A^2(x)$ exists. The second term is estimated in Eq. (E-11), where it is shown that it is of order of $\delta|\ln\delta|$. The last term is calculated explicitly, and it is of order of unity. Neglecting small contributions into the coefficient $\Gamma_1^{(2)}$, we obtain

$$\Gamma_1^{(2)} = \frac{16}{729}\sqrt{\frac{\pi}{6}}\delta^4. \tag{F-15}$$

For any integer $m \ge 3$, the coefficient

$$\Gamma_1^{(m)} = \int_0^\infty A_1^m(\frac{x}{\delta}) \exp\Big(-\frac{3x^2}{2}\Big) x^4 dx$$

reads

$$\Gamma_1^{(m)} = \delta^4 \int_0^\infty \beta_m(\frac{x}{\delta}) \exp\Big(-\frac{3x^2}{2}\Big) dx,$$

where $\beta_m(x) = A_1^m(x)x^4$. As $A_1^m(x)$ is an even continuous function, and it decreases being proportional to x^{-2m} as $x \to \infty$, the Fourier transform $\hat{\beta}_m(s)$ exists of the function $\beta_m(x)$. Evaluating the integral by analogy with Eq. (B-3), we find the leading term in the expression for $\Gamma_1^{(m)}$,

$$\Gamma_1^{(m)} = \delta^5 \int_0^\infty A_1^{(m)}(x) x^4 dx. \tag{F-16}$$

It follows from Eqs. (F-1) and (F-14) to (F-16) that

$$\Gamma_1 = \frac{2}{81}\sqrt{\frac{2\pi}{3}}\delta^2\Big[1 + \frac{4}{9}\mu_1\delta^2 + \frac{81}{2}\sqrt{\frac{3}{2\pi}}\frac{\delta^3}{\mu_1}\int_0^\infty \sum_{m=3}^\infty \Big(\mu_1 A_1(x)\Big)^m x^4 dx\Big].$$

Combining this equality with Eq. (F-11) and returning to the initial notation, we arrive at the formula

$$\Gamma_1 = \frac{2}{81}\sqrt{\frac{2\pi}{3}}\delta^2\Big[1 - \frac{4}{9}\mu\delta^2 + \frac{81}{2}\sqrt{\frac{3}{2\pi}}\mu^2\delta^3\int_0^\infty \frac{A_1^3(x)x^4}{1+\mu A_1(x)}dx\Big]. \qquad \text{(F-17)}$$

To assess the coefficient Γ_2, we use Eqs. (25), (26) and (F-13) and obtain (up to terms of higher order of smallness)

$$0 \le \Gamma_2 \le \int_0^\infty A(\frac{x}{\delta})\Big(-\frac{3x^2}{2}\Big)x^4 dx = \frac{\pi\delta}{9}, \qquad \text{(F-18)}$$

which implies that the contribution of Γ_2 into the mean square end-to-end distance is negligible compared with that of Γ_1 [the integral Γ_2 is multiplied by δ^2 in Eq. (66)]. Substitution of Eq. (F-17) into Eq. (66) results in

$$\Big(\frac{B}{b}\Big)^2 = \Big(\frac{2\pi b^2}{3}\Big)^{\frac{3}{2}}C\Big\{1 - \frac{4}{27}\mu\delta^2\Big[1 - \frac{4}{9}\mu\delta^2 + \frac{81}{2}\sqrt{\frac{3}{2\pi}}\mu^2\delta^3\int_0^\infty \frac{A_1^3(x)x^4}{1+\mu A_1(x)}dx\Big]\Big\}.$$

Combining this equality with Eq. (62), we conclude that the second term in the square brackets is negligible compared with the first. Neglecting this contribution and returning to the initial notation, we arrive at Eq. (68).

To assess the integral terms in Eqs. (65) and (69), we introduce the function

$$D(\mu) = \mu\int_0^\infty \frac{A_1^2(x)x^2}{1+\mu A_1(x)}dx. \qquad \text{(F-19)}$$

If the function $A_1(x)x^2$ had been integrable, we could use the inequality

$$\frac{\mu A_1(x)}{1+\mu A_1(x)} \le 1$$

to find that $D(\mu) \le \int_0^\infty A_1(x)x^2 dx < \infty$ for any positive μ. As this is not the case, more sophisticated estimates are needed. It follows from Eqs. (62) and (D-24) that

$$A_1(x) = \frac{4}{9x^2}\Big(\frac{1}{3} - A(x)\Big).$$

Substitution of this expression into Eq. (F-19) yields

$$D(\mu) = \Big(\frac{4}{9}\Big)^2\mu\int_0^\infty \frac{(\frac{1}{3} - A(x))^2}{x^2 + \frac{4}{9}\mu(\frac{1}{3} - A(x))}dx. \qquad \text{(F-20)}$$

As the function $A(x)$ monotonically decreases with x and vanishes at $x \to \infty$, there exists an x_0 such that

$$\frac{1}{6} \le A(x) \le \frac{1}{3} \quad (0 \le x \le x_0), \qquad 0 < A(x) < \frac{1}{6} \quad (x_0 < x < \infty). \qquad \text{(F-21)}$$

We present the integral in Eq. (F-20) as the sum of two integrals: from zero to x_0, and from x_0 to infinity, and evaluate appropriate integrals separately,

$$D(\mu) = \Big(\frac{4}{9}\Big)^2\Big[D_1(\mu) + D_2(\mu)\Big], \qquad D_1(\mu) = \mu\int_0^{x_0} \frac{(\frac{1}{3} - A(x))^2}{x^2 + \frac{4}{9}\mu(\frac{1}{3} - A(x))}dx,$$

$$D_2(\mu) = \mu\int_{x_0}^\infty \frac{(\frac{1}{3} - A(x))^2}{x^2 + \frac{4}{9}\mu(\frac{1}{3} - A(x))}dx. \qquad \text{(F-22)}$$

Taking into account that in the interval $x \in [0, x_0]$,

$$x^2 + \frac{4}{9}\mu\Big(\frac{1}{3} - A(x)\Big) \geq \frac{4}{9}\mu\Big(\frac{1}{3} - A(x)\Big), \qquad \frac{1}{3} - A(x) \leq \frac{1}{6},$$

the function $D_1(\mu)$ is estimated as follows:

$$D_1(\mu) \leq \frac{9}{4}\int_0^{x_0}\Big(\frac{1}{3} - A(x)\Big)dx \leq \frac{3}{8}x_0. \tag{F-23}$$

Using the estimates in the interval $x \in (x_0, \infty)$,

$$x^2 + \frac{4}{9}\mu\Big(\frac{1}{3} - A(x)\Big) \geq x^2 + \frac{2}{27}\mu, \qquad \frac{1}{3} - A(x) \leq \frac{1}{3},$$

the function $D_2(\mu)$ is evaluated as

$$D_2(\mu) \leq \frac{\mu}{9}\int_{x_0}^{\infty}\frac{dx}{x^2 + \frac{2}{27}\mu} \leq \frac{\mu}{9}\int_0^{\infty}\frac{dx}{x^2 + \frac{2}{27}\mu} = \frac{\mu}{9}\sqrt{\frac{27}{2\mu}}\int_0^{\infty}\frac{dy}{y^2+1} = \frac{\pi}{2}\sqrt{\frac{\mu}{6}}. \tag{F-24}$$

It follows from Eqs. (F-22) to (F-24) that there are positive constants $D^{(0)}$ and $D^{(1)}$ such that for any μ,

$$D(\mu) \leq D^{(0)} + D^{(1)}\sqrt{\mu} = D^{(0)} + D^{(1)}\frac{\sqrt{\varepsilon}}{\delta\sqrt{2\pi}},$$

where notation (62) is employed. This formula implies that the integral term in Eqs. (65) and (69) obeys the inequality

$$\frac{\varepsilon}{\delta}\int_0^{\infty}\frac{A_1^2(x)x^2}{1+\mu A_1(x)}dx = 2\pi\delta\mu\int_0^{\infty}\frac{A_1^2(x)x^2}{1+\mu A_1(x)}dx \leq 2\pi D^{(0)}\delta + D^{(1)}\sqrt{2\pi\varepsilon}, \tag{F-25}$$

and it can be disregarded compared with unity.

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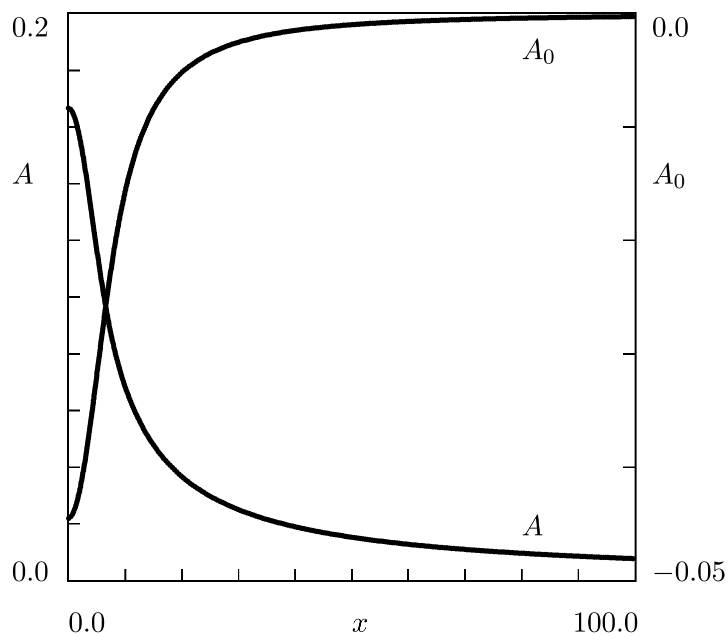

Figure 1: Graphs of the functions $A(x)$ and $A_0(x)$.